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HP-67 CALCULATOR PROGRAMS FOR THERMODYNAMIC DATA AND PHASE DIAGRAM CALCULATIONS

Leo Brewer

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by

Leo Brewer

Materials and Molecular Research Division, Lawrence Berkeley Laboratory

Department of Chemistry, University of California

Berkeley, California 94720

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THERMODYNAMIC HP67 CALCULATOR PROGRAMS

Introduction

Thermodynamic data and phase equilibria are greatly needed to meet current materials problems. Specific design criteria often require rather unique combinations of materials. Of the many combinations that might be of interest, data are available for only a small fraction. Useful combinations are often overlooked or great expense is incurred because an unnecessarily large number of combinations must be tested. The calculation of thermodynamic data and phase diagrams, even when no experimental data exist, is possible using spectroscopic levels of the gaseous atoms and chemical bonding theory (1-11). This was demonstrated for a large number of transition metal binary and multicomponent systems for which little or no data were available (2). Because of limitations of space for the large number of binary and multicomponent systems presented, projections of phase diagrams along the temperature axis were presented yielding only maximum extent of phase boundaries at the optimum temperatures although the text did discuss temperatures coefficients of the boundaries. The results of the calculations as a function of temperature will be presented in detail in subsequent publications.

The present report is a supplement to a tabulation of the thermodynamic and phase data for the 100 binary systems of Mo with the elements from H to Lr. The calculations of thermodynamic data and phase equilibria were carried out from 5000 K to low temperatures at which attainment of phase equilibria would not be practical. The results of these calculations are to be published as a special issue of the Atomic Energy Review, a publication of the International Atomic Energy Agency, Vienna. As only the results of the calculations are presented in the Atomic Energy Review issue, the present report is being used to present the methods of calculation used.

The thermodynamics involved is rather straightforward and the reader is referred to any of the advanced thermodynamic texts, e.g. Ref.(12), for derivations of the thermodynamic relations. The procedures for using chemical bonding theory to provide estimates of thermodynamic data have been outlined in previous publications (1-12).

The calculations were largely carried out using an HP-65 programmable calculator and the programs have been tabulated (13). In this report, those programs have been put in form for use with the HP-67 calculator which allows for a great reduction in the number of programs required to carry out the calculations.

It is difficult in a compendium of calculation procedures of this type to present topics in a coherent manner, but an effort has been made to assemble programs into related groups. As the equations which serve as the basis for the calculations are discussed in detail in Ref.(13), the discussion of the background equations will be limited in this report.

CHAPTER I

Data Fitting Using the Chebyshev Polynomials

A. Least-Square Fitting Using Chebyshev Orthogonal Polynomials

The Chebyshev (Tschebycheff) polynomials, $T_n(x) = \cos(n\cos^{-1}x)$, are orthogonal over the continuous interval $0 \le x \le 1$ and they have been shown to be the most economical polynomial for expressing $f(x)$ as a polynomial series with the minimum number of terms for a given accuracy.

The Chebyshev polynomial can be modified[14,15] to $C_n(\bar{x})$ which is orthogonal for discrete integer values of the variable, $\bar{x}$, from 0 to N with

$$C_o = 1 \text{ and } C_n = n!\,\Delta^n\left[\binom{\bar{x}}{n}\binom{\bar{x}+1-N}{n}\right] = \sum_{m=0}^{n}(-1)^m\binom{n}{m}\binom{n+m}{m}\frac{\bar{x}!\,(N-m)!}{(\bar{x}-m)!\,N!}$$

$$= \sum_{m=0}^{n}(-1)^m\frac{(n+m)!}{(n-m)!\,(m!)^2}\;\frac{\bar{x}!\,(N-m)!}{(\bar{x}-m)!\,N!}\;.$$

The recurrence relation is

$$C_{n+1} = [(2n+1)(N-2\bar{x})C_n - n(N+n+1)C_{n-1}]/(n+1)(N-n)$$
$$C_o = 1$$
$$C_1 = 1 - 2\bar{x}/N$$
$$C_2 = 1 + 6\bar{x}(\bar{x}-N)/N(N-1)$$

For N = 7, for example,

$$C_o = 1,\; C_1 = 1 - \tfrac{2}{7}(\bar{x}),\; C_2 = 1 - \bar{x} + \tfrac{1}{7}(\bar{x})^2\; C_3 = 1 - \tfrac{55}{21}(\bar{x}) + (\bar{x})^2 - \tfrac{2}{21}(\bar{x})^3.$$

The Chebyshev polynomials for discrete integer values are particularly useful for least square fitting of experimental data. Because of the orthogonality, cross terms are zero in the matrix used to solve the set of linear equations obtained by setting the partial derivatives of the squares of the deviations equal to zero.

Thus, the coefficients of $f(\bar{x}) = c_oC_o(\bar{x}) + c_1C_1(\bar{x}) + c_2C_2(\bar{x}) + c_3C_3(\bar{x}) + \ldots$ are readily calculated without solution of a matrix by the relation $c_n = (f,C_n)/(C_n,C_n)$ where

$$(f,C_n) = \sum_{x=0}^{N} f(x)C_n(\bar{x}) \text{ and } (C_n,C_n) = \sum_{x=0}^{N}[C_n(\bar{x})]^2 = \frac{(N+n+1)!\,(N-n)!}{(2n+1)(N!)^2}\;.$$

For N+1 values of $f(x)$ at N evenly spaced intervals of x, the values of $C_n(\bar{x})$ to be multiplied by $f(x)$ are evaluated by the following program.

$$C_{n+1} = \frac{(2n+1)(N-2\bar{x})C_n - n(N+n+1)C_{n-1}}{(n+1)(N-n)}$$

$$C_o = 1 \quad \text{and} \quad C_1 = (N-2\bar{x})/N$$

$$C_2 = \frac{3(N-2\bar{x})C_1 - (N+2)}{2(N-1)}$$

$$C_3 = \frac{5(N-2\bar{x})C_2 - 2(N+3)C_1}{3(N-2)}, \quad \text{etc.}$$

The integers, $\bar{x}$, which range from 0 to N, are related to x by $\bar{x} = (x-x_i)/I = x/I - r$, where x_i is the initial value of x and I is the interval spacing of x.

The values of $C_n(\bar{x})$ are stored in the registers starting with $C_1(1)$, $C_2(1) \cdots C_{n_{max}}(1)$, $C_1(2)$, $C_2(2) \cdots C_{n_{max}}(2)$, $C_1(3) \ldots$. In each cycle of calculations of $C_n(x)$, n is incremented until $C_{n_{max}}(x)$ has been calculated, then x is incremented and the cycle started again at n = 1. The calculation stops when x exceed N/2, as the second half of the values of $C_n(x)$ are the same as the first half except for change of sign for odd values of n. For n' = 3, there is sufficient storage to calculate the $C_n(x)$ values up to N = 15. For n' = 4, the maximum is N = 11. However, if storage is to be provided for subsequent (f,C_n) calculations, the maximum N values for n'=3 and 4 are 13 and 9, respectively.

n', the maximum value of n or the order of the polynomial used for fitting, is keyed in first. With N evenly spaced intervals of x, the number of data points to be treated, N+1, is keyed in next.

Directions:

(1) Insert tape Cheb C_n

(2) n' ↑ N+1 A 24 displayed at end of calculation

The values of $C_n(\bar{x})$ calculated in the order of increasing n for each value of $\bar{x}$ and in order of increasing $\bar{x}$ are stored in the registers in reverse order from index number 24 to 7. If it is desired to examine the $C_n(\bar{x})$ values, R/S following the calculations of step 2 will display 24 $C_1(1)$, 23 $C_2(1)$, 22 $C_3(1)$, 21 $C_1(2)$, etc. Only the contents of registers with non-zero values are displayed. When no non-zero values remain, 6 followed by 24 will be displayed (See Ref. 23).

If it is desired to preserve the $C_n(\bar{x})$ values for future (f,C_n) calculations, key f W/DATA and insert data card. Values of $C_n(\bar{x})$ are also tabulated for several values of N and n in Ref.(13) and could be keyed in for calculation of (f,C_n) values by Prgm. Cheb (f,C_n).

Prgm. Cheb C_n

(2)	fLBLA	1	-	STO5	hR↓	1	-	STO6	2	5	
	hSTI	0	STO4								13
	fLBL0	RCL5	2	÷	RCL4	1	+	gx>y	GTO2	STO4	
	1	STO3	RCL4	2	X	RCL5	÷	CHS	1	+	
	fDSZ	STO(i)									35
	fLBL1	RCL4	2	X	RCL5	-	X	RCL3	2	X	
	1	+	X	hx⇄y	RCL3	X	RCL5	1	+	RCL3	
	+	X	+	RCL3	RCL5	-	÷	RCL3	1	+	
	÷	fDSZ	STO(i)	RCL6	RCL3	1	+	gx>y	GTO0	STO3	
	hR↓	hR↓	fISZ	RCL(i)	hx⇄y	fDSZ	GTO1				82
	fLBL2	2	STO÷5	gLBLfe	RCL5	fINT	STO4	2	4	hSTI	
	hRTN	6	STO6	fLBLC	RCL(i)	fx≠0	GTOD	fDSZ	GTOC	fLBLD	
	hRCI	DSP0	hPSE	RCL(i)	gx=y	GTOfe	DSP2	f-x-	fDSZ	GTOC	112

R	3	4	5	6	I	Values of $C_n(\bar{x})$ are stored in reverse order from E to A, S9 to S0, and 9 to 7.
	n=1 to n'-1	$\bar{x}$=0 to $N_{int}\frac{N}{2}$	N $\frac{N}{2}$	n'-1	Index	

Test:

(2) n'=3 ↑ No. of data pts.=14 A, 24 after 40 sec.

R/S 24, $C_1(1)$ = 0.85; 23, $C_2(1)$ = 0.54; 22, $C_3(1)$ = 0.08;
21, $C_1(2)$ = 0.69; 20, $C_2(2)$ = 0.15; 19, $C_3(2)$ = -0.46;
18, $C_1(3)$ = 0.54; 17, $C_2(3)$ = -0.15; 16, $C_3(3)$ = -0.69;
15, $C_1(4)$ = 0.38; 14, $C_2(4)$ = -0.38; 13, $C_3(4)$ = -0.66;
12, $C_1(5)$ = 0.23; 11, $C_2(5)$ = -0.54; 10, $C_3(5)$ = -0.47;
9, $C_1(6)$ = 0.08; 8, $C_2(6)$ = -0.62; 7, $C_3(6)$ = -0.17; 6, 24.

The least square fit to the starting data with terms ranging in n up to the maximum value, n', yields the equation $f(x) = \sum_{n=0}^{n'} [(f,C_n)/(C_n,C_n)]\, C_n(\bar{x})$, which has the advantage over equations fit by other least-square procedures in not weighting the different powers unequally. Unless weighting factors are added, all points will have equal weight. The equation can be expanded in powers of $\bar{x}$ by substitution of

$$C_n(\bar{x}) = \sum_{m'=0}^{n} (-1)^{m'} \frac{(n+m')!\ \bar{x}!\,(N-m')!}{(n-m')!\,(m'!)^2(\bar{x}-m')!N!} .$$

Each $C_n(\bar{x})$ will provide n terms in powers of $\bar{x}$ ranging from $(\bar{x})^o$ to $(\bar{x})^{m'}$. Substitution of $\bar{x} = x/I - r$ will then convert each term to m' terms in x^m ranging from x^o to $x^{n'}$. The final equation will be a polynomial $f(x) = \sum_{m=0}^{n'} a_m x^m$. Each of these coefficients relate to the original (f,C_n) terms by $a_m = \sum_{n=m}^{n'} b_{mn}(f,C_n)$. For n' = 3, there will be ten b_{mn} coefficients. For n' = 4, there will be fifteen b_{mn} coefficients to be evaluated, multiplied by the appropriate (f,C_n) values and summed to obtain the a_m values.

The b_{mn} coefficients are evaluated by the equation

$$b_{mn} = \frac{1}{(C_n,C_n)} \frac{1}{(-I)^m} \sum_{m'=m}^{n} A_{m'n} R_{m'm}$$

where $(C_n,C_n) = \dfrac{(N+n+1)!\,(N-n)!}{(2n+1)(N!)^2}$

and $A_{m'n} = \dfrac{(n+m')!\,(N-m')!}{(n-m')!\,(m'!)^2 N!}$

<u>For m = n</u>, m'=m=n, R = 1 and $A = \dfrac{(2n)!\,(N-n)!}{(m!)^2 N!}$.

Thus $b_{mn} = \dfrac{(2n!)^2(N-n)!}{(n!)^2(N!)(-I)^n(C_n,C_n)}$ for m=n.

<u>For m = n-1</u>, $b_{n-1,n} = (b_{nn})(-In)(N/2 + r)$

<u>For m = 0</u>, $R_{m'o} = r(r+1) \ldots (r + m' - 1)$ and $b_{on} = \dfrac{1}{(C_n,C_n)} \sum_{m'=0}^{n} A_{m'n} R_{m'o}$

<u>For m' = m+1</u>, $R_{m'm} = m'r + \frac{1}{2}m'(m'-1)$

<u>For m = 1, m' = 3</u>, $R_{m'm} = 3r^2 + 6r + 2$

<u>For m = 1, m' = 4</u>, $R_{m'm} = 2(2r^3 + 9r^2 + 11r + 3)$

<u>For m = 2, m' = 4</u>, $R_{m'm} = 6r^2 + 18r + 11.$

Values of b_{00}, b_{01}, b_{11}, b_{02}, b_{12}, b_{22}, b_{03}, b_{13}, b_{23}, and b_{33} are tabulated for n=3 and N = 4, 7 and 8, and 9 and equations as a function of N are given in Table I-5 of Ref.(13).

When values of f(x) are given for x values that are evenly spaced at N intervals of magnitude I starting with an initial value x_i, Prgm. Cheb(f,C_n) will convert to variable $\bar{x} = x/I - x_i/I = x/I - r$ with $\bar{x}$ varying by integral values from 0 to N and then will least-square fit $f(\bar{x})$ to a Chebyshev polymomial of order n' using the b_{mn} coefficients of Prgm. Cheb C_n corresponding to n' and N as discussed in Ref.(13). If followed by Prgm. Cheb-a, the Chebyshev polynomial is expressed as $f(x) = \sum_0^{n'} a_n x^n$ upon insertion of I and $r = x_i/I$. The following program is designed for n' = 3, but can be adapted to n' = 4. $i\frac{N}{2}$ is integer value of $\frac{N}{2}$.

Directions:

(1) Insert Cheb (f,C_n) Prgm.

(2) Insert Cheb C_n Data Tape for n'=3 and appropriate N

			Display
(3)	f(0)	B	f(0)
(4)	f(1)	R/S	f(1)
	f(2)	R/S	f(2)
	⋮	⋮	⋮
	$f(i\frac{N}{2}-1)$	⋮	$f(i\frac{N}{2}-1)$
	$f(i\frac{N}{2})$	⋮	When N odd, $f(i\frac{N}{2})C_3(i\frac{N}{2})$; otherwise $\frac{N}{2}$
	$f(i\frac{N}{2}+1)$	⋮	$-f(i\frac{N}{2}+1)$
	$f(i\frac{N}{2}+2)$	⋮	$-f(i\frac{N}{2}+2)$
	⋮	⋮	⋮
	f(N-1)	R/S	-f(N-1)
(5)	f(N)	E	(f,C_0)
			(f,C_1)
			(f,C_2)
			(f,C_3)

Start at step 3 for each new set of data with same N. Step 5 must be keyed before starting again at step 3. For different N start at step 2.

Test:

(2) Insert Cheb C_n Data tape for n'=3 and N+1=14 data points.

(3) 4B; 15 R/S; 40 R/S; 85 R/S; 156 R/S; 259 R/S; after each of these steps, the input number used in the calculation is displayed; 400 R/S - 67.133; 585 R/S; 820 R/S; 1111 R/S; 1464 R/S; 1885 R/S; 2380 R/S; after each of these steps, the negative of the input number is displayed;

(5) 2955 E 12159, -7483, 2632, -408.

Prgm. Cheb(f,C_n)

	gLBLfe	RCL5	fINT	STO4	2	4	hSTI	hRTN			8
(3)	fLBLB	STO0	STO1	STO2	STO3	hRTN					14
(4)	gLBLfc	↑	↑	↑	fGSB3	fGSB5	hx⇄I	hR↑	hRTN	RCL4	
	fx=0	GTOfb	hR↓	GTOfc	fLBLfb	hR↓	GTOfd				31
	fLBL3	STO+0	fGSB4	STO+1	fGSB4	STO+2	fGSB4	STO+3	hRTN		40
	fLBL4	CLx	RCL(i)	fDSZ	X	hRTN					46
	fLBL5	4	hx⇄I	gDSZ(i)	hRTN	fGSB6	hx⇄I	hRTN			54
	fLBL6	hx⇄I	fISZ	RCL5	RCL5	fINT	gx≠y	hRTN	hRCI	3	
	+	hSTI	hRTN								67
	gLBLfd	fGSB7	fGSB8	hR↑	hRTN	GTOfd					73
(5)	fLBLE	fGSB7	STO+0	hR↓	STO+1	hR↓	STO+2	hR↓	STO+3	gGSBfe	
	RCL0	RCL1	RCL2	RCL3	gSTK	hRTN					89
	fLBL7	CHS	↑	CHS	↑	CHS	↑	CHS	hRTN		98
	fLBL8	STO+0	fGSB9	STO+3	fGSB9	STO+2	fGSB9	STO+1	hRTN		107
	fLBL9	CLx	RCL(i)	fISZ	X	hRTN		113 memory steps.			

R	0	1	2	3	4	5	I
	(f,C_0)	(f,C_1)	(f,C_2)	(f,C_3)	x Index	$\frac{N}{2}$	C_n Index

$C_n(x)$ values in E to A, S9 to 0, and P9 to 7.

Directions:

(1) Insert Cheb-a tape

(2) Insert (f,C_0) to (f,C_3) in registers 0-3 if not carried over from Prgm. Cheb.(f,C_n).

		Display
(3)	I ↑ r A	a_0
(4a)	SST	a_1
(4b)	SST	a_2
(4c)	SST	a_3

(5) x B → f(x); E → f(x+I); E → f(x+2I), etc.

NOTE: After step 4c, the a_n values can be reviewed by keying another SST which will flash the four a_n values in the order a_0 to a_3. The (f,C_n) values are retained in R0-3 and step 3 can be repeated after N/2 STO 5; for example, if incorrect values of I or r are used.

Test:

(2) 12159 STO0, 7483 CHS STO1; 2632 STO2; 408 CHS STO3; 6.5, STO5;

(3) 200 ↑ 1.5 A 0.625; (4) SST 0.00375; SST -1.25×10^{-5} SST 1.25×10^{-7}

(5) 300 B 4; E15, E40, E85; 1500 B 400, E585, E820.

Prgm. Cheb-a

(3)	fLBLA	STOE	hR↓	CHS	STOC	RCL5	2	X	STOD	3	
	STOA	STOB	fGSB1	RCL3	STO6	X	STO9	fGSB2	RCL3	X	
	STO8	2	STOA	STOB	fGSB1	RCL2	STO5	X	STO+8	fGSB2	
	RCL2	X	STO7	3	STOA	STOB	fGSB0	STOX6	RCLE	3	
	X	6	+	RCLE	X	2	+	fGSB3	2	STOB	
	RCLE	X	1	+	fGSB3	+	1	STOB	fGSB3	+	
	RCLC	÷	RCL6	hSTI	X	STO+7	1	STOA	fGSB1	RCL1	
	X	STO+7	fGSB2	RCL1	X	STO6	RCLD	1	+	h1/x	
	RCL0	X	STO+6	2	STOA	fGSB0	STOX5	RCLE	fGSB3	1	
	+	2	STOB	hR↓	RCLE	1	+	RCLE	X	STO4	
	fGSB3	+	RCL5	X	STO+6	3	STOA	RCL4	fGSB3	1	
	STOB	+	RCLE	fGSB3	+	3	STOB	hR↓	RCLE	2	
	+	RCL4	X	fGSB3	+	hRCI	X	STO+6	RCL6	hRTN	
(4)	RCL7	RCL8	RCL9	gSTK							134
	fLBL2	fGSB1	RCLC	X	RCLA	X	RCLD	2	÷	RCLE	
	+	X	hRTN								147
	fLBL1	fGSB0	fGSB3	RCLC	RCLA	hy^x	÷	hRTN			155
	fLBL0	RCLD	hN!	gx^2	RCLD	RCLA	−	hN!	÷	RCLD	
	RCLA	+	1	+	hN!	÷	RCLA	2	X	1	
	+	X	hRTN								178
	fLBL3	RCLD	RCLB	−	hN!	X	RCLD	hN!	÷	RCLA	
	RCLB	+	hN!	X	RCLA	RCLB	−	hN!	÷	RCLB	
	hN!	gx^2	÷	hRTN							202
(5)	fLBLE	hR↑	RCLC	−	fLBLB	↑	↑	↑	RCL9	X	
	RCL8	+	X	RCL7	+	X	RCL6	+	hRTN		221

R	0	1	2	3	4	5	6	7	8	9
	(f,C_0)	(f,C_1)	(f,C_2)	(f,C_3)	r^2+r	N 2 (f,C_2) $(f,C_2)/(C_2,C_2)$	(f,C_3) $(f,C_3)/(C_3,C_3)$ a_0	a_1	a_2	a_3

R	A	B	C	D	E	I
	n	m'	−I	N	r	4 or 5 $(f,C_3)/(C_3,C_3)$

The three programs Cheb-C_n, Cheb-(f,C_n), and Cheb-a can be combined in several ways. There is enough space on one tape to combine the first two programs for a total of 204 memory steps if the 8 steps of gLBLfe are not duplicated; thus there would be no need to put the $C_n(x)$ values on a data tape. However, if N+1, the number of data points, is frequently used, it would save time to have stored the $C_n(x)$ values on a tape rather than to recalculate each time. If a data tape is used for the $C_n(x)$ values, a portion of Prgm. Cheb-a can be added to the end of Prgm.Cheb-(f,C_n).

This would provide enough space for the following additions for calculation of df(x)/dx and $\int_0^x f(x)dx$ upon keying xC and xD, respectively, or following xB with R/S to obtain df(x)/dx and another R/S to obtain the integral.

hR↑	fLBLC	↑	↑	RCL9	3	X	X	RCL8	2
X	+	X	RCL7	+	hRTN	hR↑			
fLBLD	↑	↑	RCL9	4	÷	X	RCL8	3	÷
+	X	RCL7	2	÷	+	X	RCL6	+	X
hRTN									

It is unusual to have thermodynamic data of sufficient accuracy to warrant more than the four constant fit of Prgm. Cheb-a. Prgm. Cheb-C_n already can accommodate quartic or higher power fits. Prgm. Cheb-(f,C_n) and Cheb-a could be expanded to a quartic fit if desired.

For most applications of Prgms. Cheb C_n, Cheb(f,C_n), and Cheb-a, the same number of data points, N+1, would not be repeatedly used and there would be no need to store the constants from the Cheb C_n calculations. Then Cheb C_n and Cheb(f,C_n) would be combined on the same tape and the instructions would be simplified to the following:

Directions:

		Display
(1)	Insert Cheb C_n-Cheb(f,C_n) tape	
(2)	n'=3 ↑ N+1 A	24
(3)	f(0) B	f(0)
(4)	f(1) R/S	f(1)
	f(2) R/S	f(2)
	⋮ ⋮	
	f(N-1) R/S	-f(N-1)
(5)	f(N) E	(f,C_0),(f,C_1),(f,C_2),(f,C_3)
(6)	Insert Cheb-a tape	
(7)	I ↑ r A	a_0
(8)	SST SST SST	a_1,a_2,a_3
(9)	x B →f(x); E → f(x+I); E → f(x+2I), etc.	

TEST: (Continuation of Prgm. Cheb C_n test at top of pg. 8)

(7) 10 ↑ 1 A 1; (8) SST .1, SST .01, SST .001; (9) 10 B 4, E15, E40.

Chapter II

Fitting of Experimental Data by An Analytical Function

Two types of operations will be considered. The first type requires a very accurate fit in a limited range of x for interpolation purposes, with no smoothing of the data. The second type smooths the data to fit some predetermined functional form by a least-square procedure. The first type will be discussed first and illustrated with some examples.

A. Interpolation Fit to $f(x) = \Sigma a_n x^n$

Program Interp. GK fits four (x,y) pairs with the x values at evenly spaced intervals of magnitude I to a cubic polynomial, or any three pairs to a quadratic equation, or any two pairs to a linear equation, which can be used for interpolation purposes. The calculations are outlined in Ref.(13). In addition, the program is specifically designed to accept values of $-(G^o-H^o_{Std})/RT$ or $-(G^o-H^o_{Std})/T$ for each of the reactants and products of a chemical reaction at two, three or four temperatures and fit the resulting $-(\Delta G^o-\Delta H^o_{Std})/RT$ values to an interpolation equation which can then be combined with ΔH^o_{Std} or $\Delta H^o_{Std}/R$ for the reaction to calculate ln K or K, the equilibrium constant of the reaction, at desired temperatures.

Directions:

(1) Insert tape Interp.GK

			Display
	2 Pt. Fit		
(2a)	$y_1 \uparrow y_2$	A	y_1-y_2
(3a)	$x_1 \uparrow x_2$	R/S	a_0
(4a)	SST		a_1
(5)	x E		y
	3 Pt. Fit		
(2b)	$y_1 \uparrow y_2 \uparrow y_3$	B	y_1-y_2
(3b)	$x_1 \uparrow x_2 \uparrow x_3$	R/S	a_0
(4b)	SST SST		a_1,a_2
(5)	x E		y
	4 Pt. Fit		
(2c)	$y_1 \uparrow y_2 \uparrow y_3 \uparrow y_4$	C	I^3a_3
(3c)	$I \uparrow x_1$	R/S	a_0
(4c)	SST SST SST		a_1,a_2,a_3
(5)	x E		y

For the reaction aA + bB = mM + nN + oO, the values of $g = -(G^o - H^o_{Std})/RT$ (a positive number) for the reactants and products are keyed in as follows:

		Display
(a)	fc to initiate a complete set of data	0.00
(b)	g_A ↑ a X g_B ↑ b X D	0.00
(c)	g_M ↑ mX g_N ↑ n X g_O ↑ o X R/S	$-(\Delta G^o - \Delta H^o_{Std})/RT$, 0.00

Steps b and c are repeated at each temperature. If only one mole of a reactant or product appears in the equation, e.g. n=1, omit n X and merely key g_N ↑. After the values at each of the temperatures have been entered, the following steps are carried out depending upon whether a 2, 3 or 4 pt. fit is desired.

		Display
(d)	f a	$-(\Delta G^o - \Delta H^o_{Std})/RT$ at 4th temperature or zero if less than 4 temperatures treated.
(e_4)	For 4 pt. fit: key C and then continue with steps 3c,4c,and 5.	$I^3 a_3$
(e_3')	For 3 pt. fit: key f b	$-(\Delta G^o - \Delta H^o_{Std})/RT$ at third temperature
(e_3'')	B	$y_1 - y_2$
	<u>Continue with steps 3b, 4b, and 5.</u>	
(e_2')	For 2 pt. fit: key f b twice.	$-(\Delta G^o - \Delta H^o_{Std})/RT$ at second temperature
(e_2'')	A	$y_1 - y_2$
	<u>Continue with steps 3a,4a,and 5.</u>	

After the values of $-(\Delta G^o - \Delta H^o_{Std})/RT$ have been fit to either a linear, quadratic or cubic equation for interpolation purposes, the following steps yield values of lnK or K.

		Display
(6)	$-\Delta H^o_{Std}/R$ STO 6	$-\Delta H^o_{Std}/R$
(7)	T f d	ln K
(8)	SST	K

NOTE 1: A new set of data cannot be treated unless step d has been carried out followed by step a. The program will accommodate an equation with three different products or four products if there is only one mole of the last product value entered. There can be two different reactants or three if there is only one mole of the last reactant value entered. However, any number of products and reactants can be accommodated if + is keyed in after the second reactant entry and every subsequent one and if + is keyed in after the third product entry and every subsequent one.

NOTE 2: The program can be used for $-(G^{o}-H^{o}_{Std})/T$ and ΔH^{o}_{Std} as well as for the dimensionless quantities used to illustrate the displays, but step 7 will display R lnK instead of lnK and it must be divided by R before obtaining K by step 8. R in appropriate units can be stored in register D for use with step 7 or RCL D STO÷0 STO÷1 STO÷2 STO÷3 will convert the equation for $-(\Delta G^{o}-\Delta H^{o}_{Std})/T$ to the dimensionless $-(\Delta G^{o}-\Delta H^{o}_{Std})/RT$ form: so that it is unnecessary to divide by R each time step 7 is carried out. Of course, the appropriate $-\Delta H^{o}_{Std}$ or $-\Delta H^{o}_{Std}/R$ must be used.

NOTE 3: The values of $-(\Delta G^{o}-\Delta H^{o}_{Std})/RT$ obtained at each temperature are stored in the secondary registers starting with SO during the calculations following step d. Thus, a set of values at four temperatures is available for repeat fits using two, three or four of the temperatures. For each fit, after the first, key fP⇄S and go to step d and then continue with either step e_4, e_3, or e_2 depending upon which fit is desired. Step d returns the values to the secondary registers and they are available for repeated use. Although the program will not fit more than values for four temperatures at a time, steps a-c can be carried out repeatedly for up to ten temperatures. Any two, three, or four of these values can be recalled and stored in the stack as one would do to initiate steps 2a, 2b, or 2c. After fP⇄S to safeguard the values for future use, one would then proceed with steps 2 to 4 for the particular fit chosen. Also as discussed in Note 4, this procedure requires keying of hSF0 if steps a to c are to be used again. Steps a to c can also be used to evaluate $\Delta H^{o}_{Std}/R$ of the reaction from the enthalpies of formation of the reactants and products. One should use fP⇄S appropriately to insure that values of $-(\Delta G^{o}-\Delta H^{o}_{Std})/RT$ or values of a_n that are wanted for subsequent calculations are not erased by the ΔH calculations.

NOTE 4: Flag 0 is used to control the index numbers that regulate the storing of values during steps a to c. The program sets F0 when inserted and subsequent operation of the program maintain F0 in the proper set or cleared position as needed. However, if the use of steps a to c is not subsequently followed by step d, the next operation of steps a to c will not start storage in R0 but will store beyond the last registers used.

<u>Test</u>:

(2b) 1.978 ↑ 2.536 ↑ 3.25 B -0.558;

(3b) 0.3 ↑ 0.4 ↑ 0.5 R/S 1.240;

(4b) SST 0.120 SST 7.800; (5) 0.4 E 2.536;

(2c) 1.552 ↑ 1.978 ↑ 2.536 ↑ 3.25 C 0.004;

(3c) 0.1 ↑ 0.2 R/S 1.000

(4c) SST 2.000 SST 3.000 SST 4.000; (5) 0.4 E 2.536

cont'd.

$C(gr) + 2Cl_2(g) = CCl_4(g)$ (a) fe 0.00

500	(b_1) 1.16 ↑ 49.85 ↑ 2 X D 0.00;	(c_1) 68.1 R/S - 32.76, 0
1000	(b_2) 2.78 ↑ 55.43 ↑ 2 X D 0.00;	(c_2) 81.31 R/S - 32.33, 0
1500	(b_3) 4.19 ↑ 58.85 ↑ 2 X D 0.00;	(c_3) 90.01 R/S - 31.88, 0
2000	(b_4) 5.38 ↑ 61.34 ↑ 2 X D 0.00;	(c_4) 96.53 R/S - 31.53, 0
K		

(d) f a - 31.530; (e_4) C - 0.020; (3c) 500 ↑ 500 R/S - 33.050;

(4c) SST 3.60×10^{-4} SST 5.20×10^{-7} SST - 1.60×10^{-10}; (5) EEX 3 E - 32.330;

1.98719 STOD, $-\Delta H^{o}_{o}/R = 25\times10^{3}$ RCLD ÷ = 12581 STO6

RCLD 1.98719 STO÷0 STO÷1 STO÷2 STO÷3

		ln K			K
(7)	500 fd	8.676		(8) SST	5858
	750 fd	0.392			1.479
	EEX3 fd	-3.689			2.50×10^{-2}
	1500 fd	-7.656			4.73×10^{-4}
	2EEX3 fd	-9.576			6.94×10^{-5}

fP⇄S f a -31.530; f b - 31.880; (2b) B - 0.430; (3b) 500 ↑ EEX3 ↑ 1500 R/S - 33.170; (4b) SST 8.0×10^{-4} SST 4.0×10^{-8};

RCLD 1.98719 STO÷0 STO÷1 STO÷2

(7)	500 fd	8.676	5858
	750 fd	0.395	1.485
	1500 fd	-7.656	4.73×10^{-4}

fP⇄S fa - 31.530; fb - 31.880 fb - 32.330; (2a) A - 0.403; (3a) 500 ↑ EEX 3 R/S - 33.190; (4a) SST 8.6×10^{-4} (5) EEX 3 E - 32.330;

RCLD 1.98719 STO÷0 STO÷1

(7)	750 fd	0.397	1.487
	1500 fd	-7.666	4.69×10^{-4}

Prgm. Interp.GK

(d)	gLBLfa	RCL0	RCL1	RCL2	RCL3	fP⇄S	hSF0	hRTN			8
(e,f)	fLBLfb	hR↓	hRTN								11
(2a)	fLBLA	STO4	−	0	STO2	STO3	hR↓	hRTN			19
(3a)	STO5	−	÷	STO1	RCL5	X	CHS	RCL4	+	STO0	
(4a)	hRTN	RCL1									31
(2b)	fLBLB	hx⇄y	−	STO5	hR↓	hLSTx	STO4	−	0		
	STO0	STO3	hR↓	hRTN							44
(3b)	STO9	hR↓	STO8	hR↓	STO7	RCL8	−	÷	RCL8	RCL9	
	+	STOB	X	RCL7	RCL8	+	RCL5	X	RCL9	RCL8	
	−	STOA	÷	−	RCL9	RCL7	−	÷	STO1	RCL5	
	RCLA	÷	−	CHS	RCLB	÷	STO2	RCL8	E	CHS	
(4b)	RCL4	+	STO0	hRTN	RCL1	RCL2					90
(2c)	fLBLC	hR↑	STOC	−	STO7	hR↓	hLSTx	−	STO5	hR↓	
	hLSTx	−	STO4	RCL7	3	÷	RCL4	+	RCL5	−	
	2	÷	hRTN								113
(3c)	STOB	hR↓	STOA	3	hy^x	÷	STO3	RCLB	RCLA	+	
	X	3	X	CHS	RCL5	RCL4	2	X	−	2	
	÷	RCLA	gx^2	÷	+	STO2	RCL4	RCLA	÷	RCLA	
	RCLB	2	X	+	RCL2	X	−	RCLA	RCLB	+	
	RCLB	X	3	X	RCLA	gx^2	+	RCL3	X	−	
	STO1	0	STO0	RCLB	E	CHS	RCLC	+	STO0	hRTN	173
(4c)	RCL1	RCL2	RCL3								176
(7,8)	gLBLfd	E	RCL6	hR↑	÷	+	hRTN	ge^x			184
(5)	fLBLE	↑	↑	↑	RCL3	X	RCL2	+	X	RCL1	
	+	X	RCL0	+	hRTN						199
(a)	gLBLe	0	↑	↑	↑	hF?0	hSTI	hRTN			207
(b)	fLBLD	+	+	STO(i)	CLX	hRTN					213
(c)	+	+	+	RCL(i)	−	STO(i)	fISZ	hCF0	f-x-	fe	
	hRTN							224 memory steps.			224

2 pt. R	0	1	2	3	4	5
(2a-4a)	a_0	a_1	0	0	y_2	x_2

3 pt. R	0	1	2	3	4	5	6	7	8	9
(2b-4b)	0	a_1	a_2	0	y_2	y_3-y_2		x_1	x_2	x_3
	a_0									
	A	B								
	x_3-x_2	x_2+x_3								

4 pt. R	0	1	2	3	4	5	7
(2c-4c)	$0, a_0$	a_1	a_2	a_3	y_2-y_1	y_3-y_1	y_4-y_1
	A	B	C				
	I	x_1	y_1				

R	0 to 3	4	5	6	7	8	9
	Each a_n is in R_n	y_2 or y_2-y_1	used	$\Delta H^o_{Std}/R$	x_1 or y_4-y_1	0 or x_2	0 or x_3

R	A	B	C	I
	x_3-x_2 or I	x_2+x_3 or x_1	0 or y_1	Index

RS 0-3 store $-(\Delta G^o-\Delta H^o_{Std})/RT$ for 2 to 4 temperatures in order of increasing temperature.

B. Least-Square Fitting of Data to an Analytical Function

Least-square fitting of data to an equation $y = f(x)$ is not a routine process but requires careful consideration of the variations of errors in y as a function of x.[15,16,17] For example, if it were desired to obtain the values of c and d in the expression $y = cx^2 + dx^3$ that best represent a set of data, one could least-square a variety of functions of y. The use of the unweighted function would tend to heavily weight values of y at large x. As just one alternative example, one could least-square $y/x^2 = c + dx$ and obtain, in general, quite different values of c and d that would correspond to more heavy weighting of values of y at low x than for the previous procedure.

One should carefully consider the magnitude of errors in y as a function of x before selecting the appropriate procedure. One should apply appropriate weighting to off-set any bias of the least-square procedure as well as to attempt to correct for systematic errors.[17]

The first example will be the fitting of a set of data (x,y) to a three constant equation, $y = a + bf_1(x) + cf_2(x)$. To minimize $[y-a-bf_1(x)-cf_2(x)]^2$, one takes partial derivatives with respect to a, b and c and sets them equal to zero to obtain

$$\begin{aligned} ia &+ \Sigma f_1(x)b &+ \Sigma f_2(x)c &= \Sigma y \\ \Sigma f_1(x)a &+ \Sigma[f_1(x)]^2 b &+ \Sigma f_1(x)f_2(x)c &= \Sigma y f_1(x) \\ \Sigma f_2(x)a &+ \Sigma f_1(x)f_2(x)b &+ \Sigma[f_2(x)]^2 c &= \Sigma y f_2(x) \end{aligned}$$

where the sums are over the i values of x.

Directions:

			Display
(1)	Insert tape LSf(x)		
(2)	GTO f d W/PRGM, key in $f_1(x)$, SST SST, Key in $f_2(x)$, RUN		
(3)	A		
(4)	x_i B	repeat 4 & 5 for all i	$f_1(x)$
(5)	y_i R/S		$y_i f_2(x_i)$
(6)	R/S		a
(7)	SST SST		b,c
(8)	x C		y

NOTE: Return to step 3 for each new set of data. To add more data after step 7, RCL3 STOX5 and start at step 4 again.

Test:

$f_1(x) = \ln x$, $f_2(x) = x^{-1}$

(2) W/PRGM f LN SST SST h 1/x RUN; (3) A

(4') 1 B 0.000; (5') 20.0 R/S 20.000

(4") 10 B 2.303; (5") 15.605 R/S 1.561

(4'") EXX2 B 4.605; (5'") 19.310 R/S 0.193

(6) R/S 10.000; (7) SST 2.000 SST 10.000 (8) 10 C 15.605

Prgm. LSf(x)

(3)	fLBLA	fCLREG	fP⇄S	fCLREG	hRTN						5
(4)	fLBLB	↑	↑	↑	fe	hR↑	fd	Σ+	hLSTx	hRTN	15
(5)	fLBL1	STO+5	X	STO+6	hR↓	hLSTx	X	STO+7	hRTN		24
(6)	RCLΣ+	STO1	hR↓	STO2	fP⇄S	RCL9	RCL8	RCL7	RCL5	fP⇄S	
	STO8	hR↓	STO9	hR↓	STO4	hR↓	STO3	RCL1	gx^2	RCL3	
	STO÷5	÷	RCL8	−	RCL1	RCL2	RCL3	÷	X	RCL4	
	−	STO8	hx⇄y	STO4	RCL2	gx^2	RCL3	÷	RCL9	−	
	STO9	RCL6	RCL7	RCL5	RCL2	X	hx⇄y	−	hSTI	RCL5	
	RCL1	X	hR↑	−	STO0	RCL4	RCL9	X	RCL8	gx^2	
	−	RCL0	RCL9	X	RCL8	hRCI	X	−	hx⇄y	÷	
	STOB	RCL4	X	RCL0	hx⇄y	−	RCL8	÷	STOC	RCL2	
	X	RCL1	RCLB	X	+	RCL3	÷	RCL5	hx⇄y	−	
	STOA	hRTN	RCLB	RCLC							118
(7)	fLBLC	↑	↑	fe	RCLC	X	hx⇄y	fd	RCLB	X	
	+	RCLA	+	hRTN							132
	gLBLfd	[	$f_1(x)$	]	hRTN						
	gLBLfe	[	$f_2(x)$	]	hRTN	136 memory steps + $f_1(x)+f_2(x)$					

R	0	1	2	3	4	5	6	7	8	9
	t	$\Sigma f_1(x)$	$\Sigma f_2(x)$	i	$\Sigma f_1(x)f_2(x)$	Σy	$\Sigma y f_1(x)$	$\Sigma y f_2(x)$	$\Sigma[f_1(x)]^2$	$\Sigma[f_2(x)]^2$
					q	$\frac{1}{i}\Sigma y$			s	r

RS	4	5	6	7	8	9	A	B	C	I
	$\Sigma f_1(x)$	$\Sigma[f_1(x)]^2$	$\Sigma f_2(x)$	$\Sigma(f_2(x)]^2$	$\Sigma f_1(x)f_2(x)$	i	a	b	c	u

$$q = \frac{1}{i}(\Sigma f_1(x))^2 - \Sigma(f_1(x))^2, \quad r = \frac{1}{i}(\Sigma f_2(x))^2 - \Sigma(f_2(x))^2,$$

$$t = \frac{\Sigma y \Sigma f_1(x)}{i} - \Sigma y f_1(x), \qquad u = \Sigma y \Sigma f_2(x)/i - \Sigma y f_2(x)$$

Linear Regression

For a simple linear regression to fit a set of (x,y) to f(y)=bf(x)+a, the following program is adapted from program Stat 1-22 of the HP-65 User's Library (18). f(x) may be 1/x and f(y) may be ln y or more complicated functions. In the equations for the coefficient of determination and for the standard errors, f(x) will be taken as x and f(y) will be taken as y. The coefficient of determination is given by

$$r^2 = \frac{[\Sigma xy - (\Sigma x \Sigma y)/i]^2}{[\Sigma x^2 - (\Sigma x)^2/i][\Sigma y^2 - (\Sigma y)^2/i]} .$$

The standard error estimate of y on x is given by

$$s_{y \cdot x} = \left[\frac{\Sigma(y-\hat{y})^2}{i-2}\right]^{\frac{1}{2}} = \left[\frac{\Sigma y^2 - a\Sigma y - b\Sigma xy}{i-2}\right]^{\frac{1}{2}} .$$

The standard error of a is given by

$$s_a = s_{y \cdot x}\left[\frac{\Sigma x^2}{i\Sigma x^2 - (\Sigma x)^2}\right]^{\frac{1}{2}} .$$

The standard error of b is given by

$$s_b = s_{y \cdot x}[\Sigma x^2 - (\Sigma x)^2/i]^{-\frac{1}{2}} .$$

Directions:

(1) Insert tape LR

(2) Key GTO fb W/PRGM, key f(x) SST SST, key f(y) SST SST, key $f^{-1}(y)$ RUN. If f(x) = x or f(y) = y, nothing need be keyed in for f(x) or for f(y) and $f^{-1}(y)$.

(3)	fa	
(4)	$x_1 \uparrow y_1$ E	1
	$x_2 \uparrow y_2$ E	2
	⋮	⋮
	$x_n \uparrow y_n$ E	n
(5)	A	a
	SST	b
(6)	B	r^2
(7)	xC	$\hat{y}$
(8)	D	$s_{y \cdot x}$
	R/S	s_a
	SST	s_b

NOTE 1: For data at regular intervals, after fLBLE add hLSTx $f^{-1}(x)I$ + hx⇄y gLBLe and after fLBLC add hR↑ I_1+ ↑ ↑ ↑ gLBLc where I is the interval between x values and $f^{-1}(x)$ converts f(x) to x. Step 4 is changed to x_1 ↑ y_1 fe, y_2 E, y_3 E ... y_n E and step(5) is changed to x_1 ↑ ↑ ↑ fc → y_1, C → y_2, C → y_3 ... C → y_n.

Prgm. LR

fLBLE	fd	hx⇄y	fb	Σ+	hRTN					6
gLBLa	fCLREG	fP⇄S	hRTN							10
fLBLA	fP⇄S	RCL8	RCL4	RCL6	X	RCL9	÷	−	STOC	
RCL5	RCL4	gx^2	RCL9	÷	−	STOD	÷	STOB	fP⇄S	
$f\bar{x}$	RCLB	X	−	STOA	hRTN	RCLB				37
fLBLB	RCLB	RCLC	X	fP⇄S	RCL7	RCL6	gx^2	RCL9	÷	
−	÷	fP⇄S	hRTN							51
fLBLC	fb	RCLB	X	RCLA	+	fGSBO	hRTN			59
fLBLD	fP⇄S	RCL7	RCL6	RCLA	X	−	RCL8	RCLB	X	
−	RCL9	2	−	÷	$f\sqrt{x}$	hRTN				76
RCL5	RCL9	fP⇄S	÷	RCLD	÷	$f\sqrt{x}$	X	↑	↑	
RCLD	$f\sqrt{x}$	÷	hx⇄y	hRTN	hx⇄y					92

gLBLb[f(x)]hRTN
gLBLd[f(y)]hRTN
fLBLO[f^{-1}(y)]hRTN

R	4	5	6	7	8	9
	$\Sigma f(x)$	$\Sigma(f(x))^2$	$\Sigma f(y)$	$\Sigma(f(y))^2$	$\Sigma f(x)f(y)$	i

R	A	B	C	D
	a	b	$\Sigma f(x)f(y)-(\Sigma f(x)\Sigma f(y)/i$	$\Sigma(f(x))^2-(\Sigma f/(x))^2/i$

Test:

(2) GTO fb W/PRGM h1/x SST SST fLN SST SST ge^x RUN

(3) fa (4) 1300 ↑ 1.47×10^{-2} E 1, 1400 ↑ 2.63×10^{-2} E2, 1500 ↑ 4.5×10^{-2} E3, 1600 ↑ 6.96×10^{-2}E

(5) A, a=4.112 SST, b = −10835 (6) B 0.9998

(7) 1300 C 1.466×10^{-2}, 1600 C 6.99×10^{-2}

(8) D, $s_{lny,1/x}$ = 0.0124; R/S s_a = 0.08; SST s_b = 745.

Least-Square Fit of $f(y) = af_1(x) + bf_2(x) + cf_3(x)$

Prgm. $LSf_1f_2f_3$ is an extension of Prgm. LSf(x).

$$a = (A\Sigma yf_1 - q\Sigma f_1f_2 + r\Sigma f_1f_3)/D$$
$$b = (q\Sigma f_1{}^2 - B\Sigma yf_1 + s\Sigma f_1f_3)/D$$
$$c = (-r\Sigma f_1{}^2 - s\Sigma f_1f_2 + C\Sigma yf_1)/D$$

where
$$A = \Sigma f_2{}^2\Sigma f_3{}^2 - (\Sigma f_2f_3)^2$$
$$B = \Sigma f_1f_2\Sigma f_3{}^2 - \Sigma f_1f_3\Sigma f_2f_3$$
$$C = \Sigma f_1f_2\Sigma f_2f_3 - \Sigma f_1f_3\Sigma f_2{}^2$$
$$D = A\Sigma f_1{}^2 - B\Sigma f_1f_2 + C\Sigma f_1f_3$$
$$q = \Sigma yf_1\Sigma f_3{}^2 - \Sigma yf_3\Sigma f_2f_3$$
$$r = \Sigma yf_2\Sigma f_2f_3 - \Sigma yf_3\Sigma f_2{}^2$$
$$s = \Sigma yf_3\Sigma f_1f_2 - \Sigma yf_2\Sigma f_1f_3$$

If f_1, f_2, and f_3 are not functions of x directly but are functions $f(x')$ of $x' = f'(x)$, the program provides for conversion of x to x'. For example, if a solidus or liquidus curve is to be expressed as a function of T_{MP}-T rather than T, $f'(x)$ would be keyed in as T_{MP}-CHS. After insertion of a set of data, additional data can be added after steps (5)-(7); follow with steps (5)-(6) for new values of a, b, and c.

Directions:

(1) Insert tape $LSf_1f_2f_3(x)$

(2) Key GTO fa W/PRGM, key in $f'(x)$ SST SST SST, key in $f_1(x)$ SST SST, key in $f_2(x)$ SST SST, key in $f_3(x)$ SST SST, key in f(y) SST SST, key in $f^{-1}(y)$ RUN. If any $f(x) = x$ or $f(y) = y$, key in nothing for that function.

		Display
(3)	A (before a set of data to clear registers)	
(4)	$x_i \uparrow y_i$ B repeat for all i.	$f_1(x)f_3(x)$
(5)	C	a
(6)	SST SST	b,c
(7)	x D	$\hat{y}$
(8)	(x_1-100) STOE $E \rightarrow y_1$, $E \rightarrow y_2$, etc for x at 100 intervals.	

LS$f_1f_2f_3$(x)

(3)	fLBLA	fCLREG	fP⇄S	fCLREG	hRTN						5
(4)	fLBLB	fd	STOA	hR↓	fa	STOB	RCLA	X			
	STO+1	hR↓	↑	fb	STOC	RCLA	X	STO+2	hR↓		
	RCLC	RCLB	Σ+	hR↓	hR↓	fc	STOD	RCLA	X	STO+3	
	RCLC	RCLD	fP⇄S	Σ+	fP⇄S	hLSTx	RCLB	X	STO+0	hRTN	42
	gLBLa	f'(x)	↑	↑	↑	f_1(x)	hRTN				
	gLBLb	f_2(x)	hRTN								
	gLBLc	f_3(x)	hRTN								
	gLBLd	f(y)	hRTN								
	gLBLe	f^{-1}(y)	hRTN							55+f( )	
(5)	fLBLC	fP⇄S	RCL5	RCL8	fP⇄S	STO9	hR↓	STO6	RCL7	RCL5	
	X	RCL8	gx^2	−	STOA	RCL9	RCL5	X	RCL0	RCL8	
	X	−	STOB	RCL9	RCL8	X	RCL0	RCL7	X	−	
	STOC	RCL0	X	RCL6	RCLA	X	+	RCL9	RCLB	X	
	−	STOD	RCL2	RCL8	X	RCL3	RCL7	X	−	STOE	
	RCL0	X	RCL2	RCL5	X	RCL3	RCL8	X	−	hSTI	
	RCL9	X	−	RCLA	RCL1	X	+	RCLD	÷	STOA	
	RCL3	RCL9	X	RCL2	RCL0	X	−	STO4	RCL0	X	
	RCLB	RCL1	X	−	hRCI	RCL6	X	+	RCLD	÷	
	STOB	RCLC	RCL1	X	RCL4	RCL9	X	−	RCLE	RCL6	
(6)	X	−	RCLD	÷	STOC	RCLA	hRTN	RCLB	RCLC	164+f(x)	
(7)	fLBLE	RCLE	EEX	2	+	STOE	fLBLD	fa	RCLA	X	
	STO4	hR↓	↑	fb	RCLB	X	STO+4	hR↓	↑	fc	
	RCLC	X	STO+4	RCL4	fe	hRTN				190+f(x)	

P	0	1	2	3	4	5	6	7	8	9
	Σf_1f_3	Σyf_1	Σyf_2	Σyf_3		Σf_3^2		Σf_2^2	Σf_2f_3	i
					s		Σf_1^2			Σf_1f_2

S					5		7	8	9
					Σf_1^2		Σf_2^2	Σf_1f_2	i

Reg.	A	B	C	D	E	I
	f(y)	f_1(x)	f_2(x)	f_3(x)		
	A	B	C	D		
	a	b	c		r	q

TEST:

(2) GTO f a W/PRGM 3 EEX 3 − CHS SST SST SST SST SST gx^2 SST SST 3 h y^x SST SST h 1/x SST SST h 1/x RUN

(3) A (4) 1800 ↑ 2.2894×10^{-4} B 2.07×10^{12}; 1900 ↑ 2.7465×10^{-4} B 1.46×10^{12}; 2EEX 3 ↑ 3.333×10^{-4} B 1×10^{-12}; 2100 ↑ 4.1×10^{-4} B 6.56×10^{11}; 2200 5.1234×10^{-4} B 4.1×10^{11}

(5) C, 0.992 (6) SST 1.016×10^{-3} SST 9.92×10^{-7}; (7) 2200 D 5.1235×10^{-4}; 1800 D 2.2894×10^{-4} (8) 1700 STOE E 2.2894×10^{-4} E 2.7464×10^{-4} 3.333×10^{-4} E 4.100×10^{-4} E 5.1235×10^{-4}.

The common practice of high precision fitting of experimental data with a power series with a large number of terms is not followed here. The experimental error inherent in most data do not warrant high precision fits and the use of a large number of terms that work against one another makes it impossible to assign physical significance to any term. When the data have been made available at even intervals, the use of orthogonal functions such as the Chebyshev polynomials of Chapter 1 to fit $f(y) = \sum_n a_n[f(x)]^n$ offers many advantages. The orthogonality makes the solution of matrices simple and a change in the number of terms does not change the coefficients of the earlier terms. However, there are often theoretical reasons to expect a better fit with a mixture of functions such as lnx with powers of x as well as inverse powers of x. Then $f(y) = a + bf_1(x) + cf_2(x)$ or $f(y) = af_1(x) + bf_2(x) + cf_3(x)$ can be fit using the previous programs. The next section describes ways of using additional functions without increasing the number of independent parameters.

Fit of Data to Equations with More Than Three Constants

The solution of simultaneous equations with more than three variables requires 4×4 and higher matrices. If the data are available at even spaced x values, a much simpler procedure involves the use of orthogonal polynomials such as the Chebyshev polynomials. Such a simpler procedure is to use interpolation programs to provide data for evenly spaced x values and to fit the data with a Chebyshev polynomial as illustrated in Chapter I.

Sometimes, it is desired to fit data to a four constant equation, but it may not be advisable to fit an equation with four simultaneously adjustable constants, as errors in the data can yield quite unreasonable constants when the four terms are allowed to work against one another in an attempt to fit the scattered data. A procedure for fitting the four constants with only three being independently adjusted will be illustrated for heat capacity data and for values of enthalpy increments available from drop-calorimeter measurements. The equation $C_p = a + bT + cT^{-2}$ is often adequate for many substances for a considerable temperature range above room temperature and can be fit as described for a three constant fit. The negative cT^{-2} term represents the drop in heat capacity at lower temperatures due to quantized vibrational levels. The 'a' term corresponds to the classical Dulong and Pettit value.

The 'bT' arises from electronic, thermal expansion and anharmonicity contributions. These contributions also provide higher order terms which together with a contribution from vacancy formation necessitate a dT^2 term at higher temperatures. The enthalpy equation corresponding to $C_p = a + bT + cT^{-2} + dT^2$ is $H_T - H_{T_{Std}} = a(T-T_{Std}) + \frac{1}{2}b(T^2-T_{Std}^2) - c(T^{-1}-T_{Std}^{-1}) + (d/3)(T^3-T_{Std}^3)$. As the enthalpy data often have approximately the same percent error over the temperature range of study, the expression to be fitted by least-square procedures is often

$$(H_T-H_{T_{Std}})/(T-T_{Std}) = a + \tfrac{1}{2}b(T+T_{Std}) + c/TT_{Std} + (d/3)(T^2+TT_{Std}+T_{Std}^2).$$

If both the 'c' and 'd' terms are important, there will be a minimum value of dC_p/dT at $(T^*)^4 = -3c/d$ with the contribution of the dT^2 term becoming very small at lower temperatures and with the contribution of the cT^{-2} term becoming very small at higher temperatures. A first approximation to T* can be obtained from inspection of the data. A revised value can be selected upon examination of the deviations between observed and calculated C_p values near T*. A practical way of treating the data is to replace the constant d by $-3c/(T^*)^4$ to obtain $C_p = a + bT + c[T^{-2}-3(T^*)^{-4}T^2]$. One could also replace c to obtain $C_p = a + cT + d[T^2-\frac{1}{3}(T^*)^4T^{-2}]$. The equations are equivalent. Program LSf(x) can be used with $f_1(x) = T$ and $f_2(x) = T^{-2} - 3(T^*)^{-4}T^2$ if the constant c is retained or with $f_2(x) = T^2 - \frac{1}{3}(T^*)^4T^{-2}$ if the constant d is retained. Program LSC_p^* is given here with the constant c retained.

Directions:

		Display
(1)	Insert tape LS C_p^*	
(2)	T* A	T*
(3)	T B } repeat for all data	T
(4)	C_p R/S }	C_p $f_2(x)$
(5)	R/S	a
(6)	SST SST SST	b,c,d
(7)	T C	C_p
(8)	T_i ↑ H_i-H_{298} fa	T_i
(9)	T D	$H-H_i$
(10)	R/S	$H-H_{298}$

NOTE: If T_i = 298.15, key H_i-H_{298} = 0 in step 8. Start at step 2 for each new set of data. To add more data after step 6, RCL3 STOX5 and start with step 3 again.

Test:

(2) 740 A; (3) 500 B; (4) 1.35 R/S 2.0×10^{-6}; EEX3 B; 2.9 R/S - 2.6×10^{-5}; 1500 B; 4.7056 R/S - 1.0×10^{-4}; 2EEX 3 B; 6.975 R/S - 2.8×10^{-4}

(5) R/S 0.999; (6) SST 0.001001, SST -.99932; SST 0.9998×10^{-6}

(7) 500 C 1.350; (8) 298.15 ↑ 0 fa 298.15; (9) 500 D 179.9 (10) R/S 179.9

Prgm. LS C_p^*

(2)	fLBLA	fCLREG	fP⇄S	fCLREG	STOE	hRTN				6
(3)	fLBLB	↑	↑	↑	fe	hR↑	Σ+	hLSTx	hRTN	15
(4)	STO+5	X	STO+6	hR↓	hLSTx	X	STO+7	hRTN		23
(5)	The next 91 steps are unchanged from Prgm. LSf(x) through STOA (steps 25-115)									
	RCLC	CHS	3	X	RCLE	4	hy^x	÷	STOD	hx⇄y
(6)	hRTN	RCLB	RCLC	RCLD						128
	gLBLfe	RCLE		4	hy^x	3	hx⇄y	÷	CHS	
	hx⇄y	gx^2	X	hLSTx	h1/x	+	hRTN			143
(7)	fLBLC	↑	↑	↑	RCLD	X	RCLB	+	X	RCLC
	hR↑	gx^2	÷	+	RCLA	+	hRTN			160
(8)	gLBLa	STOO	hR↓	hSTI	hRTN					165
(9)	fLBLD	↑	↑	↑	hRCI	+	X	hRCI	gx^2	+
	RCLD	X	3	÷	RCLC	hRCI	÷	hR↑	÷	+
	hR↑	hRCI	+	RCLB	X	2	÷	+	RCLA	+
	hR↑	hRCI	-	X	hRTN	RCLO	+	hRTN	203 memory steps.	

Registers are the same as for LSf(x) except for H_i-H_{298} in O and for A-I.

A	B	C	D	E	I
a	b	c	d	T*	u
					T_i

Program LS C_p^* can be readily adapted to the fit of $(H_T-H_{T_i})/(T-T_i)$ values to the constants a, b, c and d.

$$(H_T-H_{T_i})/(T-T_i) = a' + b'T + c'f(T) \qquad \text{where}$$

$$a' = a + \tfrac{1}{2}bT_i - cT_i^2(T^*)^{-4} = a + \tfrac{1}{2}bT_i + \tfrac{1}{3}dT_i^2$$

$$b' = \tfrac{1}{2}b - cT_i(T^*)^{-4} = \tfrac{1}{2}b + \tfrac{1}{3}dT_i$$

$$c' = -c(T^*)^{-4} = \tfrac{1}{3}d$$

$$f(T) = T^2 - (T^*)^4/TT_i$$

Directions:

		Display
(1)	Insert tape LS H*	
(2)	T* ↑ T_i ↑ H_i-H_{298} A	T*
(3)	T B } repeat for all data	T
(4)	$H-H_i$ R/S } repeat for all data	$f_2(T)(H-H_i)/(T-T_i)$
(5)	R/S	d
(6)	SST SST SST	c,b,a
(7)	T C	C_p
(8)	T D	$H-H_i$
(9)	R/S	$H-H_{298}$

Test:

(2) 740 ↑ 298.15 ↑ 0 A 740

(3) 500 B; (4) 180 R/S - 1570828; EEX 3 B; 1246.5 R/S - 10220;
1500 B; 3130 R/S 4113513; 2EEX3 B; 6030 R/S 12391015;

(5) R/S 9.9997×10^{-7} (6) SST - 99953, SST 0.001000, SST 1.00048;

(7) 500 C 1.35; 500 D 180; R/S 180

Prgm. LS H*

(2)	fLBLA	fCLREG	STO0	hR↓	fP⇄S	fCLREG	hSTI	hR↓	STOE	hRTN
(3)	fLBLB	↑	↑	↑	fe	hR↑	Σ+	hLSTx	hRTN	19
(4)	STO0	CLx	hRCI	-	RCL0	hx⇄y	÷	hR↑	hx⇄y	
	STO+5	X	STO+6	hR↓	hLSTx	X	STO+7	hRTN		36
(5)	The next 91 steps to STOA are unchanged from Prgm.LSf(x) except for changing hSTOI and hRCI to STO6 and RCL6 at steps 73 and 90.									
	RCLC	3	X	STOD	RCLB	RCLC	hRCI	X	-	RCLB
	STO1	hx⇄y	2	X	STOB	hR↓	hRCI	X	RCLA	STO0
	-	CHS	STOA	RCLE	4	hy^x	RCLC	X	CHS	STOC
	RCLB	hx⇄y	RCLD	hRTN	hR↓	hR↓	hR↓			164
(8)	fLBLD	RCL1	hx⇄y	X	hLSTx	fe	hLSTx	f√x	hx⇄y	RCLD
	X	3	÷	hx⇄y	hR↓	+	RCL0	+	hR↑	hRCI
	-	X	hRTN	fP⇄S	RCL0	fP⇄S	+	hRTN		192
	gLBLfe	RCLE	↑	4	hy^x	hRCI	÷	hx⇄y	÷	CHS
	hLSTx	gx^2	+	hRTN						206
(7)	fLBLC	↑	↑	h1/x	gx^2	RCLC	X	hx⇄y	RCLB	X
	+	RCLA	+	hRTN			220 memory steps.			

All registers are the same as for LSf(x) except that u is stored in R6, H_i-H_{298} in S0, a' is added to R0, b' is added to R1 and A to I are as follows:

A	B	C	D	E	I
a'	b'	c'	d	T*	T_i
a	b	c			

Program LSf(x) and the related programs fit data to a three constant equation. To least-square fit the two constant $y = bf_1(x) + cf_2(x)$ equation, it is necessary to minimize $\Sigma[y - bf_1(x) - cf_2(x)]^2$ to obtain the two equations: $b\Sigma f_1^2 + c\Sigma f_1 f_2 = \Sigma y f_1$ and $b\Sigma f_1 f_2 + c\Sigma f_2^2 = \Sigma y f_2$. Simultaneous solution yields $b = (\Sigma y f_1 \Sigma f_2^2 - \Sigma y f_2 \Sigma f_1 f_2)/D$ and $c = (\Sigma y f_2 \Sigma f_1^2 - \Sigma y f_1 \Sigma f_1 f_2)/D$ where $D = \Sigma f_1^2 \Sigma f_2^2 - (\Sigma f_1 f_2)^2$. With $f_1(x) = x^0$, the above equations would also fit to a equation with a constant term plus a function of x. However, program SD-03A of the HP-67 Standard Pac(18)covers several of the commonly used simple functions such as $y = a + bx$, $y = ae^{bx}(a>0)$, $y = a + b\ln x$, and $y = ax^b(a>0)$.

A program based on the above equations for a two constant fit is given here to deal with properties of binary solutions as a function of molefraction, x, which varies from 0 to 1. The properties C_p, H, S and G are expressed[12] as functions of x in the following manner:

$\bar{Y}_1 = bx_2^2 + cx_2^3$, $\bar{Y}_2 = (b + \frac{3}{2}c)x_1^2 - cx_1^3$, and $Y = x_1x_2(b + \frac{1}{2}c + \frac{1}{2}cx_2)$.

In many solutions, the change from an excess of one component to an excess of the other component changes the character of the interaction and the constants of the function.[19] Thus, it is often expedient to fit each portion of the composition range independently with the change often at the midpoint, but frequently at other compositions depending upon the orbitals being utilized as one metal is added to another. When a single equation is not used over the entire composition range for partial molal quantities, a constant of integration of the Gibbs-Duhem equation must be evaluated at the overlapping composition for $\bar{Y}_1$ at high x_2 or for $\bar{Y}_2$ at high x_1 to assure continuity of the functions. The programs given below provide for evaluation of the constant of integration when necessary.

Because of occurrence of substantial systematic errors in many data, complications in the character of the interactions, and inherent bias of the least-square process when applied to the functions of interest, suitable weighting of the data is very important. A variety of weighting procedures are used. Key A makes a least-square fit to $\bar{Y}_1 = bx_2^2 + cx_2^3$, which heavily weights values at high x_2. Key B uses $\bar{Y}_1/x_2 = bx_2 + cx_2^2$ to reduce the bias of the least-square process toward high x_2 values. Key C uses $\bar{Y}_1/x_2^2 = b + cx_2$ to further reduce the weight at high x_2. Components are assigned 1 and 2 so that the experimental $\bar{Y}$ is $\bar{Y}_1$. When integral quantities are available, key D fits $Y/x_1x_2 = b + \frac{1}{2}c + \frac{1}{2}cx_2$.

When a single equation for Y_1 is not used over the entire composition range, the integration of the Gibbs-Duhem equation[12] to obtain $\bar{Y}_2$ at high x_1 requires evaluation of a constant of integration which is obtained from $d = \frac{1}{4}[(b'+c')-(b''+c'')]$ where the single primes apply to the constants for the $x_2' = 0.5 - 1$ range and the double prime applies to the constants for the $x_2'' = 0 - 0.5$ range. When the change in equations is at a value of x_1 not at the midpoint, $d = x_1^2\{[b' + c'(\frac{3}{2}-x_1)] - [b'' + c''(\frac{3}{2}-x_1)]\}$ which is stored in RD for evaluation of $\bar{Y}_2$ and Y at low x_2''.

To calculate $\bar{Y}_1$, $\bar{Y}_2$ or Y given b and c, store b in RB and c in RC and steps 6 to 8 will yield the desired quanties. If necessary, d should also be stored in RD.

Directions:

		Display
(1)	Insert Prgm. LS $\bar{Y}$	
(2)	f a	
	To fit $\bar{Y}_1 = bx_2^2 + cx_2^3$	
(3a)	x_2 A } repeat for all data	x_2^2
(4a)	$\bar{Y}_1$ R/S }	$\bar{Y}_1 x_2^3$
(5)	R/S	b,c
(6)	x_2 E	$\bar{Y}_1$
(7)	R/S	$\bar{Y}_2$
(8)	R/S	Y
	Tofit $\bar{Y}_1/x_2 = bx_2 + cx_2^2$	
(3b)	x_2 B } repeat for all data	x_2
(4b)	$\bar{Y}_1$ R/S }	$\bar{Y}_1 x_2$
	Steps 5-8 as above	
	To fit $\bar{Y}_1/x_2^2 = b + cx_2$	
(3c)	x_2 C } repeat for all data	x_2
(4c)	$\bar{Y}_1$ R/S }	$\bar{Y}_1/x_2^2$
	Steps 5-8 as above	
	To fit $Y/x_1x_2 = b + \frac{1}{2}c + \frac{1}{2}cx_2$	
(3d)	x_2 D } repeat for all data	x_1
(4d)	Y R/S }	Y/x_1x_2
(5)	R/S	$b+\frac{1}{2}c$, $\frac{1}{2}c$
(5d)	R/S	c,b
	Steps 6-8 as above	

NOTE 1: For each new set of data, start at step 2.

NOTE 2: Once constants b, c, and, if necessary, d are stored, steps 6-8 can be repeated for any values of x in range of fit.

NOTE 3: For calculations of $\bar{Y}_2$ at low x_2, d is needed if the original $\bar{Y}_1$ data were not fit to a single equation for the entire composition range as explained in the text. For such a situation, follow step 6 with step 6' after evaluation of data for $x_2'' = 0$ to 0.5 range. Step (6'): (b'+c') fe will store $d = \frac{1}{4}[(b'+c')-(b''+c'')]$ in register D. When the break in the data treatment is not at x = 0.5, use equation for d in the text.

Prgm. $\bar{Y}$

(2)	gLBLfa	fCLREG	fP⇄S	fCLREG	hRTN						5
(3a)	fLBLA	↑	gx^2	X	hLSTx	Σ+	hLSTx	hRTN			13
(4a)	X	STO+1	hx⇄y	hLSTx	X	STO+2	hRTN	GTO0			21
(3b)	fLBLB	gx^2	hLSTx	Σ+	hLSTx	hRTN					27
(4b)	STO+1	X	STO+2	hRTN	GTO0						32
(3c)	fLBLC	1	Σ+	hR↓	hRTN						37
(4c)	↑	hR↓	hx⇄y	÷	STO+2	hR↑	hLSTx	gx^2	÷	STO+1	
	hRTN	GTO0									49
(3d)	fLBLD	fGSBC	↑	↑	1	−	CHS	hRTN			57
(4d)	hx⇄y	÷	STO+2	hx⇄y	÷	STO+1	hRTN				64
(5)	fLBL0	fP⇄S	RCL5	RCL8	RCL7	fP⇄S	STO5	hR↓	STO4	hR↓	
	STO3	RCL2	X	RCL1	RCL4	X	−	RCL3	RCL5	X	
	RCL4	gx^2	−	STO0	÷	STOC	RCL1	RCL5	X	RCL2	
(5d)	RCL4	X	−	RCL0	÷	STOB	f-x-	RCLC	hRTN	−	
	STOB	hLSTx	2	X	STOC	f-x-	RCLB	hRTN			112
(6)	fLBLE	STO9	gx^2	hLSTx	RCLC	X	RCLB	+	STOA	X	
	hRTN										123
(7)	1	RCL9	−	STO8	gx^2	RCLC	2	÷	RCLA	+	
	X	RCLD	+	hRTN							137
(8)	RCL9	X	hx⇄y	RCL8	X	+	hRTN				144
(6')	gLBLfe	RCLB	RCLC	+	−	4	÷	STOD	hRTN		153

R	0	1	2	3	4	5	8	9
	D	$\Sigma y f_1$	$\Sigma y f_2$	Σf_1^2	$\Sigma f_1 f_2$	Σf_2^2	x_1	x_2

RS	5	7	8	A	B	C	D
	Σf_1^2	Σf_2^2	$\Sigma f_1 f_2$		$b+\frac{1}{2}c$	$\frac{1}{2}c$	
				$b+cx_2$	b	c	d

0 0 0 0 4 6 0 4 3 5 1

The following values can be used to test Prgm. $\bar{Y}$.

x_2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\bar{Y}_1$	4	24	72	160	300	504	784	1152	1620
$\bar{Y}_2$	1134	1024	882	720	550	384	234	112	30
Y	117	224	315	384	425	432	399	320	189

As these values are derived from $\bar{Y}_1 = bx_2^2 + cx_2^3$ with b = 200 and c = 2000, any of the weighting procedures of Prgm. $\bar{Y}$ will yield b = 200 and c = 2000.

CHAPTER III

Standard Thermodynamic Calculations

A. Thermodynamic Properties of Gases

The several programs tabulated here are designed to calculate the translational, electronic, vibrational and rotational contributions to the thermodynamic functions of gaseous molecules using the equations given in Chapter 27 of Ref.(12). For gaseous atoms, Prgm. E-A provides the electronic and translational contributions to the thermodynamic functions. It can also be used to calculate only the electronic contribution for either atoms or molecules.

Program D-LT calculates the translational, rotational and vibrational contributions for diatomic or linear polyatomic molecules. Program Cor calculates the corrections to the results of Prgm. D-LT if the effects of anharmonicity, centrifugal stretching and vibration-rotation interaction are to be included. When it is desired to obtain moments of inertia for the rotational calculations from molecular constants, Prgm. ID can be used to calculate B_e values for diatomic or linear molecules, moments of inertia or products of moments of inertia for a variety of molecules including bent triatomic, symmetric top CBA_3, octahedral BA_6, etc. Program NL uses the product of the moments of inertia of non-linear molecules to calculate the translation, rotational and vibrational contributions.

The spectroscopic constants used should be expressed in units of cm^{-1}, the unit conventionally used in spectroscopic publications. All the thermodynamic quantities are calculated in dimensionless form, which is most suitable for direct calculation of equilibrium constants. However, the programs provide for multiplication by R in appropriate units to yield the functions in the units desired.

In identifying quantities, the subscripts e, r, t and v are used to refer to electronic, rotational, translational and vibrational contributions, respectively. The superscript $^{\circ}$ for quantities including translational contributions indicate that the values are for the gaseous standard state, although the superscript is not always shown, as all values are for the gaseous standard state.

Diatomic or Linear Polyatomic Gases

Program D-LT uses the rotational constants B_e and α, the symmetry number σ, the vibrational constants w_e and $x_e w_e$, and the molecular weight M. The calculations using the equations on pp. 420-30 of Ref.(12) proceed as follows with $y = hc(B_e - \frac{1}{2}\alpha)/kT$ and $u = hc(w_e - 2x_e w_e)/kT$.

$C_{r,t}/R = \frac{7}{2} + y^2/45$, $S_{r,t}/R = \frac{7}{2} - \ln y\sigma - y^2/90 + \frac{3}{2}\ln M - 3.665 + \frac{5}{2}\ln T$,

$-(G-H_o)_{r,t}/RT = S_{r,t}/R + y/3 + y^2/45 - \frac{7}{2}$,

$(H_{298}-H_o)_{r,t}/R = 298.15(\frac{7}{2} - \frac{1}{3}y_{298} - \frac{1}{45}y_{298}^2)$,

$-(G-H_{298})_{r,t}/RT = -(G-H_o)_{r,t}/RT + (H_{298}-H_o)_{r,t}/RT$,

$(H-H_o)_{r,t}/RT = \frac{7}{2} - \frac{1}{3}y - \frac{1}{45}y^2$

$(H-H_{298})_{r,t}/R = [(H-H_o)_{r,t}/RT - (H_{298}-H_o)_{r,t}/RT]T$ with $-(H_{298}-H_o)_{r,t}/RT$ obtained by subtracting $-(G-H_{298})_{r,t}/RT$ from $-(G-H_o)_{r,t}/RT$ stored in the stack.

$C_v/R = u^2e^u/(e^u-1)^2$, $-(G-H_o)_v/RT = -\ln(1-e^{-u})$,

$(H-H_o)_v/RT = u/(e^u-1)$, $S_v/RT = (H-H_o)_v/RT - (G-H_o)_v/RT$,

$(H_{298}-H_o)_v/R = (uT)/(e^{u_{298}}-1)$, $-(G-H_{298})_v/RT = -(G-H_o)_v/RT + (H_{298}-H_o)_v/R$

$(H-H_{298})_v/R = T[(H-H_o)_v/RT - (H_{298}-H_o)_v/RT]$.

The various contributions to S/R, C_p/R, $-(G-H_{298})/RT$, $(H-H_{298})/R$ and $(H_{298}-H_o)/R$ are summed and are finally stored in registers 5 to 9, respectively.

Directions:

(1a) Insert Tape D-LT

(1b) Insert Data Tape D-LT

	Diatomic Gas	Display
(2)	M ↑ B_e ↑ α ↑ σ A	1.5 lnM-3.665
(3)	w_e ↑ $x_e w_e$ B	uT
(4)	T C	C_p^o/R
(5)	R/S	S^o/R
		$-(G^o-H_{298}^o)/RT$
		$(H_o^o-H_{298}^o)/R$
(6)	SST	$(H_{298}^o-H_o^o)/R$
(7)	R D	C_p^o
(8)	R/S	S^o
		$-(G^o-H_{298}^o)/T$
		$H^o-H_{298}^o$

cont'd.

cont'd. from p. 1

Triatomic Linear Gas		Display
(2)	$M \uparrow B_e \uparrow \alpha \uparrow \sigma$ A	1.5 lnM-3.665
(3)	$w_e' \uparrow x_e w_e'$ B	$u'T$
(3a)	$w_e'' \uparrow x_e w_e''$ f b	$u''T$
(3b)	$w_e''' \uparrow x_e w_e'''$ f b	$u'''T$ (doubly degenerate bend)
(4T)	T E	C_p^o/R

(5-8) same as for diatomic gas.

NOTE 1: After constants are entered, start at step 4 or 4T for each temperature. After completing calculations for one molecule, go back to step 1b before entering constants for new molecule. However, entering f P⇄S RCL 2 STO A RCL 3 h STI f P⇄S or entering 3.665 STO A 1.4388 h STI will replace step 1b and allow starting at step 2.

NOTE 2: w_e''' must be doubly degenerate bending frequency. If α or $x_e w_e$ are not known, key zero.

NOTE 3: Step 7 can follow either step 4, 5 or 6, but step 5 can only follow step 4, step 6 can only follow step 5, and step 8 can only follow step 7.

Test for Diatomic

(2) 114.938 ↑ .314 ↑ .003 ↑ 1 A 3.452;

(3) 700 ↑ 7 B 987.017; (4) EEX 3 C 4.423

(5) R/S 32.981, 29.975, 3005.472; (6) SST 1080.765

(7) 1.98719 D 8.789; (8) R/S 65.539, 59.567, 5972.444

Test for Linear Triatomic

(2) 113.936 ↑ .211 ↑ 0 ↑ 2 A 3.438;

(3) 700 ↑ 0 B 1007.160;

(3T')650 ↑ 0 fb 935.220;

(3T''')150 ↑ 0 fb 215.820;

(4T) EEX 3 E 7.342; (5) R/S 38.822, 33.874, 4947.9

(6) SST 1527.743; (7) 1.98719 D 14.590; (8) R/S 77.146, 67.314, 9832.4.

Prgm. D-LT

Data Tape: 298.15 in E, 3.665 in A and RS2, and 1.4388 in I and RS3.

Tape D-LT

(2)	fLBLA	STOC	hR↓	2	÷	−	hRCI	X	STOB	hR↑	
	fLN	1	•	5	X	RCLA	−	STOA	hRTN		19
(3)	fLBLB	fGSB0	STOD	hRTN							23
(3T)	gLBLfb	fGSB0	hF?2	GTO1	STO0	hSF2	hRTN				30
	fLBL0	2	X	−	hRCI	X	hRTN				37
	fLBL1	STO1	hRTN								40
(4T)	fLBLE	hSF0	fGSBC	RCL0	fGSB2	STO0	fGSB3	RCL1	fGSB2	STO1	
	fGSB3	fGSB3	RCL0	fGSB2	RCL1	STO0	hR↓	STO1	hCF0	GTO4	
	fLBL2	RCLD	hx⇄y	STOD	hR↓	hRTN					66
(4)	fLBLC	fGSB5	RCLB	hx⇄y	÷	STO2	gx^2	4	5	÷	
	STO3	3	•	5	STO6	+	RCLC	RCL2	X	fLN	
	CHS	RCL6	+	RCL3	2	÷	−	RCLA	+	hRCI	
	fLN	2	•	5	X	+	Σ+	hLSTx	RCL2	3	
	÷	RCL3	+	STO3	+	RCL6	−	RCLB	3	÷	
	RCLE	÷	↑	gx^2	5	÷	+	RCL6	−	RCLE	
	X	CHS	STO9	hRCI	÷	+	STO7	−	RCL3	−	
	RCL6	+	hRCI	X	STO8						141
	fLBL3	RCLD	hRCI	÷	STO2	gx^2	hLSTx	ge^x	STO3	X	
	hLSTx	1	−	STO4	gx^2	÷	RCL3	RCL4	÷	fLN	
	STO5	RCL2	RCL4	÷	STO6	+	Σ+	RCL5	RCL2	RCLD	
	RCLE	÷	ge^x	1	−	÷	STO5	+	STO+7	−	
	RCL6	+	hRCI	X	STO+8	RCL5	hRCI	X	STO+9	hF?0	
	hRTN										192
(5)	fLBL4	RCLΣ+	STO5	hx⇄y	STO6	fLBL6	hRTN	hR↓	f-x-	RCL7	
(6)	f-x-	RCL8	hRTN	RCL9							206
	fLBL5	fP⇄S	0	STO4	STO6	fP⇄S	hR↓	hSTI	hRTN		215
(7)	fLBLD	STOX5	STOX6	STOX7	STOX8	RCL5	RCL6	GTO6			223

R	0	1	2	3	4	5	6	7	8	9
	u"T	u'"T	y	$y^2/45$	e^u-1	$-\ln(1-e^{-u})$	3.5	$\Sigma - \frac{G-H_{298}}{RT}$	$\Sigma \frac{H-H_{298}}{R}$	$\Sigma \frac{H_{298}-H_0}{R}$
	u'T	u"T		$\frac{y}{3} + \frac{y^2}{45}$		$\frac{(H_{298}-H_0)_v}{RT}$	$\frac{u}{e^u-1}$			
	u"T	u'"T	u	e^u		ΣS/R	$\Sigma C_p/R$			

R	S2	S3	S4	S6
	3.665	1.4388	ΣS/R	$\Sigma C_p/R$

R	A	B	C	D	E	I
	3.665	yT	σ	u'T u"T	298.15	1.4388
	$\left(\begin{matrix}\frac{3}{2}\ln M \\ -3.665\end{matrix}\right)$			u'"T u'T		T

Calculation of Contributions from Anharmonicity, Centrifugal Stretching and Vibration-Rotation Interaction

Program Cor provides the corrections to be applied to the thermodynamic functions calculated for a diatomic molecule by the harmonic-oscillator-rigid-rotator approximation. The initial spectroscopic values are used in units of cm^{-1}. The final results are first displayed in dimensionless form with the quantities divided by R, the gas constant. Insertion of R = 1.98719 cal/K mol or 8.3144 J $K^{-1}mol^{-1}$ will yield the values in either set of units. However, the dimensionless values are the most suitable if the values are to be used for subsequent equilibrium calculations; steps 7 and 8 can be omitted if quantities in dimensions are not needed. The calculations are based on the following equations on pp. 430-7 of Ref.(12).

$$w_o = w_e - 2x_e w_e, \qquad B_o = B_e - \tfrac{1}{2}\alpha, \qquad x = w_e x_e / w_o$$

$$u = (hc/k)w_o/T = 1.43879\ w_o/T, \qquad \gamma = B_e/w_e, \qquad \delta = \alpha/B_o = (B_e/\alpha - 0.5)^{-1}$$

$$-\left(\frac{(F-H_o)}{RT}\right)_{cor} = [\delta + 2xu/(e^u-1)]/(e^u-1) + 8\,\gamma/u$$

$$\left(\frac{H-H_o}{RT}\right)_{cor} = \{\sigma u e^u + [2ue^u-(e^u-1)](2xu)/(e^u-1)\}/(e^u-1)^2 + 8\,\gamma/u$$

$$C_{cor}/R = \{\delta u^2 e^u(e^u+1) + [2ue^u + u - 2(e^u-1)](2ue^u)(2xu)/e^u-1)\}/(e^u-1)^3 + 16\,\gamma/u$$

$$S_{cor} = (H-H_o)_{cor}/T - (F-H_o)_{cor}/T \quad .$$

Directions:		Display
(1)	Insert tape Cor	
(2)	w_e ↑ $x_e w_e$ ↑ B_e ↑ α A	$(H_{298}-H_0)_c/R$
(3)	SST	$(S_{298})_c/R$
(4)	SST	$(C_{298})_c/R$
(5)	T B	$-(G-H_{298})_c/RT$
(6)	SST will flash the following quantities sequentially	$(H-H_{298})_c/R$ S_c/R C_c/R $-(G-H_{298})_c/RT$
(7)	R C	$-(G-H_{298})_c/T$
(8)	SST	$(H-H_{298})_c$ S_c C_c $-(G-H_{298})_c/T$

NOTE: Steps 3 and 4 can be skipped if corrections to S_{298} and C_{298} are not needed. Once step 2 has been run, start at step 5 for each temperature. Steps 7 and 8 can be omitted if dimensionless quantities are adequate.

Prgm. Cor

(2)	fLBLA	STO6	hR↓	STO7	hR↓	↑	↑	2	X	hR↑
	−	CHS	1	•	4	3	8	8	hx⇄y	X
	STOA	hR↓	hLSTx	÷	STOB	hR↓	8	hx⇄y	÷	RCL7
	X	STOD	hLSTx	RCL6	÷	•	5	−	h1/x	STOC
	2	9	8	•	1	5	fGSBB	RCL7	RCL0	X
(3,4)	STOE	hRTN	RCL9	RCL8						
(5)	fLBLB	STO0	RCLA	hx⇄y	÷	STO1	↑	ge^x	STO2	1
	−	STO3	÷	2	X	RCLB	X	STO5	RCLC	+
	RCL3	÷	RCLD	RCL1	÷	+	hSTI	RCL1	RCL2	X
	STO4	2	X_2	RCL3	−	RCL5	X	RCL4	RCLC	X
	+	RCL3	gx^2	÷	RCLD	RCL1	÷	+	STO7	RCL4
	2	X	RCL1	+	RCL3	2	X	−	RCL4	X
	2	X	RCL5	X	RCLC	RCL3	2	+	X	RCL4
	X	RCL1	X	+	RCL3	3	hy^x	÷	RCLD	2
	X	RCL1	÷	+	STO8	RCL7	RCL0	X	RCLE	−
	STO5	hR↓	hRCI	RCL7	+	STO9	hx⇄y	RCLE	RCL0	÷
(6)	hRCI	+	STO6	RCL5	hR↓	hRTN	gSTK			
(7)	fLBLC	STOX5	STOX6	STOX8	STOX9	RCL5	RCL9	RCL8	RCL6	hRTN
(8)	gSTK						172 memory steps.			

R 0	1	2	3	4	5	6	7	8	9
T	u	e^u	e^u-1	ue^u	$\frac{2xu}{(e^u-1)}$	α	B_e	C/R	S/R
					$\frac{H-H_{298}}{R}$	$-\frac{(G-H_{298})}{RT}$	$\frac{(H-H_o)}{RT}$		

R	A	B	C	D	E	I
	uT	x	δ	8γ	$\frac{H_{298}-H_0}{R}$	$-\frac{(G-H_0)}{RT}$

Test:

2359.6 ↑ 14.46 ↑ 2.01 ↑ .0187 A 0.181; SST 0.001; SST 0.001

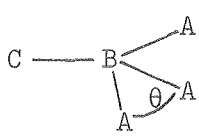
2×10^3 B 0.007; SST 23.7, 0.019, 0.030, 0.007

1.98719 C 0.0147; SST 47.1, 0.038, 0.060, 0.0147

Moments of Inertia

The moments of inertia of molecules are needed to calculate the rotational contributions to thermodynamic properties using Prgms. DLT and NL. When there is more than one value, I_S is the moment about the axis of greatest symmetry. I" indicates a doubly degenerate moment. The symmetry number, σ, is tabulated along with the equations for I. If m is the atomic weight of A and r is the internuclear distance in Å, mr^2 must be divided by 10^{16} $N_o = 6.02209\times10^{39}$ to obtain units of g cm^2. Program ID calculates $I\times10^{39}$ in g cm^2, $B_e = h/8\pi^2cI$ in cm^{-1} for linear molecules, and the product of the three principal moments of inertia, $D\times10^{117}$, for non-linear molecules. For symmetric top molecules and unsymmetric linear molecules, m_1 is atomic weight of A, m_2 of B and m_3 of C.

Diatomic A_2,	$\sigma = 2$	$I'' = \frac{1}{2}mr^2$
Linear ABA,	$\sigma = 2$	$I'' = 2mr^2$
Planar BA_3,	$\sigma = 6$	$I_S = 3mr^2$
		$I'' = \frac{3}{2}mr^2$
Tetrahedral BA_4,	$\sigma = 12$	$I = \frac{8}{3}mr^2$
Trigonal Bipyramid BA_5,	$\sigma = 6$	$I_S = 3mr^2$
		$I'' = \frac{7}{2}mr^2$
Octahedral BA_6,	$\sigma = 24$	$I = 4mr^2$
Bent BA_2,	$\sigma = 2$	$I_S = mr^2\left(2 - \frac{1+\cos\theta}{1+m_B/2m}\right)$
		$I = mr^2(1+\cos\theta)/(1+2m/m_B)$
		$I = mr^2(1-\cos\theta)$

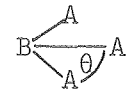
For a symmetric top 

, $\sigma = 3$, and θ in degrees.

$$I_S = 3m_1r_{12}^2(1-\cos\theta)$$

$$I'' = m_1r_{12}^2(1-\cos\theta) + \frac{m_1(m_2+m_3)r_{12}^2(1+2\cos\theta)}{3m_1+m_2+m_3}$$

$$+ \frac{m_3r_{23}}{3m_1+m_2+m_3}\left[(3m_1+m_2)r_{23} + 6m_1r_{12}\left(\frac{1\ 2\cos\theta}{3}\right)^{\frac{1}{2}}\right]$$

If $m_3 = 0$, the equations give I for the symmetric top 

, $\sigma = 3$.

If $m_1 = 0$, I" becomes the doubly degenerate moment of inertia of diatomic C-B, $\sigma = 1$.

If $\theta = 0$, I" becomes the moment of inertia of a linear triatomic molecules with atomic masses m_3, m_2 and m_1, if m_1 is divided by three at the initiation of the program.

Directions:

		Display
(1)	Insert Prgm. ID	
(2)	m ↑ r A	$mr^2/6.02209$
	Diatomic A_2	
(3D)	R/S	$I''\times10^{39}$, B_e
	Linear ABA	
(3LT)	B	$I''\times10^{39}$, B_e
	Planar BA_3	
(3P)	C	$I_S\times10^{39}$ $I''\times10^{39}$ $D\times10^{117}$
	Tetrahedral BA_4	
(3T)	D	$I\times10^{39}$ $D\times10^{117}$
	Trigonal Bypyramid BA_5	
(3TB)	E	$I_S\times10^{39}$ $I''_A\times10^{39}$ $D\times10^{117}$
	Octahedral BA_6	
(3 OC)	f a	$I\times10^{39}$ $D\times10^{117}$
	Bent Triatomic BA_2	
(3BT)	m/m_B ↑ θ f b	$I_1\times10^{39}$ $I_2\times10^{39}$ $I_3\times10^{39}$ $D\times10^{117}$
	Symmetric Top CBA_3	
(2a)	r_{12} ↑ m_1 ↑ θ f c	$I_S\times10^{39}$
(3a)	r_{23} ↑ m_3 ↑ m_2 R/S	$I''\times10^{39}$ $D\times10^{117}$
	Symmetric Top BA_3	
(2b)	r_{12} ↑ m_1 ↑ θ f c	$I_S\times10^{39}$
(3b)	0 ↑ m_2 R/S	$I''\times10^{39}$ $D\times10^{117}$
	Linear CBA	
(2c)	r_{12} ↑ m_1 f d	0
(3c)	r_{23} ↑ m_3 ↑ m_2 R/S	$I''\times10^{39}$ B_e
	Diatomic CB	
(2d)	r_{23} ↑ m_3 ↑ m_2 f e	$I''\times10^{39}$ B_e

Prgm. ID											
(2)	fLBLA	gx^2	X	6	•	0	2	2	0	9	
	STO4	÷	STOA	hRTN							14
(3D)	•	5	fGSB0	GTO1							18
(3LT)	fLBLB	2	fGSB0	fLBL1	STO0	2	•	7	9	9	
	3	2	hx⇄y	÷	STO1	hRTN					34
(3P)	fLBLC	3	fGSB0	STO0	1	•	5	fGSB0	GTO2		43
(3T)	fLBLD	8	↑	3	÷	fGSB0	↑	GTO2			51
(3TB)	fLBLE	3	fGSB0	STO0	3	•	5	fGSB0	GTO2		60
(3 OC)	gLBLfa	4	fGSB0	↑	fLBL2	STO1	gx^2	X	STO3	hRTN	
	fLBL0	RCLA	hx⇄y	X	f-x-	hRTN					76
(3BT)	gLBLfb	fCOS	1	+	STO8	hx⇄y	STO7	h 1/x	2	+	
	÷	1	-	CHS	2	X	fGSB0	STO0	RCL8	RCL7	
	2	X	1	+	÷	fGSB0	STO1	2	RCL8	-	
	fGSB0	STO2	X	X	STO3	hRTN					112
(2a-d)	gLBLfc	fCOS	STOD	hR	STO5	hx⇄y	STOE	fGSBA	1	RCLD	
	-	RCLA	X	STO6	2	X	RCLD	2	X	1	
	+	STO7	hx⇄y	STO0	hRTN						137
(3a-c)	fLBL3	STOB	hx⇄y	STOC	+	RCLA	X	RCL5	3	X	
	RCLB	+	STO8	RCLC	+	STO9	÷	RCL7	X	RCL6	
	+	hx⇄y	hSTI	hR↓	RCL7	3	÷	$f\sqrt{x}$	RCL5	X	
	6	X	RCLE	X	RCL8	hRCI	X	+	RCLC	X	
	hRCI	X	RCL9	÷	RCL4	÷	+	STO1	f-x-	gx^2	
	RCL0	X	STO3	hRTN							191
(2c)	gLBLfd	3	÷	0	gGSBfc	hRTN					197
(3c)	fGSB3	RCL1	fGSB1	hRTN							201
(2d)	gLBLfe	STOB	CLX	hR↓	STOC	CLX	hR↓	hSTI	hR↓	hR↓	
	gGSBfc	hRCI	RCLC	RCLB	fGSB3	RCL1	fGSB1	hRTN			219

R	0	1	2	3	4	5	6	7	8	9
	I"	B_e			6.022	m_1	$m_1 r_{12}^2(1-\cos\theta)$	$\frac{m}{m_B}$	$1+\cos\theta'$	$3m_1+m_2+m_3$
	I_S	I"		D						
	I_1	I_2	I_3	D				$1+2\cos\theta$	$3m_1+m_2$	

A	B	C	D	E	I
$\frac{mr^2}{6.02209}$	m_2	m_3	$\cos\theta$	r_{12}	r_{23}

Test:

(2) 10 ↑ 2 A 6.64
(3LT) B 13.28, 0.21
(3T) D 17.71, 5557.05
(3 OC) f a 26.57, 18 755.05
(2a) 2 ↑ 10 ↑ 60 f c 6.64
(2b) 2 ↑ 10 ↑ 60 f c 6.64
(2c) 2 ↑ 10 f d 0.00
(2d) 3 ↑ 30 ↑ 20 f e 17.93, 0.16

(3D) R/S 3.32, 0.84
(3P) C 19.93, 9.96, 1978.07
(3TB) E 19.93, 23.25, 10 769.50
(3BT) .1 ↑ 60 f b 11.62, 8.30, 3.32, 320.52
(3a) 3 ↑ 30 ↑ 20 R/S 57.95, 22305.50
(3b) 0 ↑ 20 R/S 8.635, 495.25
(3c) 3 ↑ 30 ↑ 20 R/S 37.92, 0.07

Non-Linear Gases

Program ID calculates $D\times10^{117}$, where D is the product of the three principal moments of inertia, for a variety of non-linear molecules. The following equations from Ref.(12) are used by Prgm. NL to calculate the rotational and translational contributions to the thermodynamic functions of non-linear molecules. The symmetry numbers, σ, are available in Ref.(12) and are also listed in the discussion of Prgm. ID.

$$C^{o}_{r,t}/R = 4, \quad (H^{o}_{298}-H^{o}_{o})_{r,t}/R = 4(298.15), \quad (H^{o}-H^{o}_{298})_{r,t}/R = 4(T-298.15)$$

$$S^{o}_{r,t}/R = 4\ln T + (\tfrac{3}{2})\ln M + \tfrac{1}{2}\ln(D\times10^{117}) - \ln\sigma - 1.1823$$

$$4 + \ln 64\pi^{5} + \ln(82.057k^{3})/(h^{6}N_{o}^{\frac{5}{2}}10^{58.5}) = -1.1823$$

$$-(G^{o}-H^{o}_{298})_{r,t}/RT = S^{o}_{r,t}/R - 4(1-298.15/T).$$

The vibrational contributions are calculated using the same equations as used for Prgm. D-LT.

The program requires that the singly degenerate vibrational frequencies be inserted first followed by doubly degenerate frequencies and finally by triply degenerate frequencies. The number of frequencies of each type must be entered. i_1 is the number of singly degenerate frequencies, i_2 is the number of doubly degenerate frequencies, and i_3 is the number of triply degenerate frequencies.

Directions:

		Display
(1)	Insert tape NL	
(2)	$M \uparrow \sigma \uparrow D\times10^{117}A$	0.000
(3)	Values of w in cm^{-1} are entered on stack so that singly degenerate values are inserted first (lowest on the stack) followed by doubly and then triply degenerate values. Groups of 1,2, but not over 3 values on the stack are entered and followed by B. A maximum of 10 values can be entered.	$w_1''\uparrow w_2'\uparrow w_1'B\rightarrow0$ $w_1'''\uparrow w_2''B\rightarrow0$ or $w_2'\uparrow w_1'B\rightarrow0$ $w_2''\uparrow w_1''B\rightarrow0$ $w_1'''B\rightarrow0$
(4)	$i_1 \uparrow i_2 \uparrow i_3$ C	$10^{2}i_1 + i_2 + 10^{-2}i_3$
(5)	T D	$-(G^{o}-H^{o}_{298})/RT$
(6)	R/S	$(H^{o}-H^{o}_{298})/R$ S^{o}/R C^{o}_{p}/R
(6')	SST	$(H^{o}_{298}-H^{o}_{o})/R$

cont'd.

Directions, cont'd.

(7)	R STO B	R
(8)	E	$-(G^o-H^o_{298})/T$
(9)	R/S	$H^o-H^o_{298}$
		S^o
		C^o_p

NOTE 1: Calculations at each temperature start at step 5 once the constants have been inserted. Step 7 need not be repeated unless new constants are entered in step 2.

NOTE 2: If dimensionless quantities are not wanted, step 6 can be deleted. SST after either step 6 or step 9 will display value of $(H^o_{298}-H^o_o)/R$.

NL Test:

(2) 133.936 ↑ 2 ↑ 202.5 A 0.000;

(3) 700 ↑ 150 B 0.000; (4) 2 ↑ 0 ↑ 0 C 200.00;

(5) EEX 3 D 35.772; (6) R/S 4588.2; 40.360, 6.835, SST 1466.9;

(7) 1.98719 STO B; (8) E 71.086; (9) R/S 9117.6, 80.204, 13.583.

Prgm. NL

(2)	fLBLA	fCLREG	fP⇄S	0	hR↓	f√x	÷	fLN	CHS	hx⇄y	
	fLN	1	•	5	X	1	•	1	8	2	
	3	-	+	STOD	CLX	1	0	hSTI	CLx	hRTN	
(3)	fLBLB	1	•	4	3	8	8	X	STO(i)	fISZ	
	CLx	hR↑	CLx	hR↓	hR↓	fx=0	hRTN	GTOB			48
(4)	fLBLC	EEX	2	÷	+	hx⇄y	EEX	2	X	+	
	STOA	hRTN									60
(5)	fLBLD	STOC	fLN	4	X	RCLD	+	STO5	4	STO6	
	RCLC	X	2	9	8	•	1	5	STOE	4	
	X	STO9	-	STO8	RCLC	÷	-	STO7	RCLA	EEX	
	2	÷	fINT	f≠0	fa	RCLA	EEX	2	÷	gFRAC	
	f=0	GTO8	EEX	2	X	fINT	fb	fLBL8	RCLA	gFRAC	
	EEX	2	X	f≠0	fc	GTO7					116
	gLBLfa	1	0	hSTI	+	STO4	fLBL0	fGSB3	gx=y	hRTN	126
	GTO0										127
	gLBLfb	STO+4	fLBL1	fGSB4	fGSB3	gx=y	hRTN	GTO1			135
	gLBLfc	STO+4	fLBL2	fGSB4	fGSB4	fGSB3	gx=y	hRTN	GTO2		144
	fLBL3	fGSB4	fISZ	hRCI	RCL4	hRTN					150
	fLBL4	RCL(i)	RCLC	÷	STO0	gx^2	hLSTx	ge^x	STO1	X	160
	hLSTx	1	-	STO2	gx^2	÷	STO+6	RCL1	RCL2	÷	
	fLN	STO3	RCL0	RCL2	÷	STO1	+	STO+5	RCL3	RCL0	
	RCL(i)	RCLE	÷	ge^x	1	-	÷	STO3	+	STO+7	
	-	RCL1	+	RCLC	X	STO+8	RCL3	RCLC	X	STO+9	
	hRTN										201
(6,6')	fLBL7	RCL7	hRTN	RCL8	f-x-	RCL5	f-x-	RCL6	hRTN	RCL9	211
(8,9)	fLBLE	RCLB	STOX5	STOX6	STOX7	STOX8	GTO7				218

continued...

cont'd. from pg. 38

R	0	1	2	3	4	5	6		7	8	9
	u	e^u	e^u-1	$-\ln(1-e^{-u})$	Index limit	$\Sigma\frac{S}{R}$	$\Sigma\frac{C_p}{R}$	Σ -	$\frac{(G-H_{298})}{RT}$	$\Sigma\frac{H-H_{298}}{R}$	$\Sigma\frac{H_{298}-H_0}{R}$
		$\frac{u}{e^u-1}$		$\frac{(H_{298}-H_0)_v}{RT}$							

R	A	B	C	D	E	I	
	$i_1 0 i_2 \cdot 0 i_3$	R	T	$\begin{pmatrix} S_{r,t}/R \\ -4\ln T \end{pmatrix}$	298.15	Index	RS0-9 are available for up to 10 values of uT.

Calculation of Electronic Level Contributions to Thermodynamic Functions

Program A can be used to calculate the complete thermodynamic functions for gaseous atoms including translational and electronic contributions or it can be used to just calculate the electronic level contributions for either atoms or molecules. Degeneracies and energies of up to seventeen levels can be stored for the calculations. Although the program is intended for calculating the contribution of electronic levels to thermodynamic functions, it can be used for any internal energy levels. For example, if the vibrational or rotational levels are sufficiently perturbed to introduce significant error even after using Prgm. Cor for anharmonic and centrifugal stretching corrections, the partition function can be calculated, seventeen levels at a time, to evaluate the vibrational or rotational contributions.

The spectroscopic unit, cm^{-1}, is used for the energies. The thermodynamic functions are calculated in dimensionless units, which are most appropriate for equilibrium calculations, but insertion of the gas constant R in appropriate units will provide the thermodynamic functions in the same units. The calculations follow the equations on pp. 422-4 of Ref.(12).

After energy levels and degeneracies have been stored in the preliminary steps, calculations at various temperatures commence with step(5). There are several choices in the sequence of steps following step(5). If the interest is primarily in the complete thermodynamic functions for an atom, step (5) would be followed by step(6"a) to yield $-(G^o-H^o_{298})/RT$ and then by step(6"b) if the remainder of the functions are desired in dimensionless form. If $-(G^o-H^o_{298})/T$ is desired, step (6"a) would be followed by step(7) and then by step(8) if the other functions are of interest. If values for all functions are wanted both with dimensions and in dimensionless form, the sequence after step(5) would be (6"a), (6"b), (7) and (8). If only the electronic contributions are wanted, step (5) would be followed by step(6') and then by steps (7) and (8) for values expressed in the units of the value of R introduced in step(7). If, after obtaining the electronic contributions of an atom through step(6'), the complete thermodynamic functions should also be wanted, replacement of the directions of step(6"a) by hR↓ hR↓ T STO D M D will allow calculation of the complete functions without repeating step(5). The restrictions are summarized as follows: step(8) only after (7), step(6"b) only after (6"a), step(7) after (6'),(6"a), or (6"b), step (6') only after (5), and step(6"a) only after (5) except after (6') with insertion of the special step given above.

In addition to the program tape, a data tape is used to store the following constants: 3.665 STO A, 298.15 STO B, 1438.8 STO C. These constants can be keyed in manually or by tape. If the constants have not been inserted before step 2, integers will be lacking in all of the displays of step 2.

Directions:

	Display
(1) Insert tape A and Data tape A	
(2-1) $g_1 \uparrow \varepsilon_1$ A	$1438.8\varepsilon_1 \cdot g_1 \times 10^{-2}$
(2-2) $g_2 \uparrow \varepsilon_2$ R/S	$1438.8\varepsilon_2 \cdot g_2 \times 10^{-2}$
(2-i) $g_i \uparrow \varepsilon_i$ R/S	$1438.8\varepsilon_i \cdot g_i \times 10^{-2}$
i up to 17	
(3) B	$(H_{298}-H_o)_e/R$
(4) R/S	$(S_{298}/R)_e$ $(C_{298}/R)_e$
(5) T C	$-(G-H_{298})_e/RT$
(6') R/S (not to be followed by 6a" without step given in text)	$(H-H_{298})_e/R$ S_e/R C_e/R $-(G-H_{298})_e/RT$
($6''_a$) M D ($6''_b$) R/S	$(H^o-H^o_{298})/R$ S^o/R C^o_p/R $-(G^o-H^o_{298})/RT$
(7) R E (8) R/S	$H-H_{298}$ S C_p $-(G-H_{298})/T$

NOTE 1: If a number of levels are inserted together at an average value of ε_i, the total g must not exceed 99.

NOTE 2: If values of ε_i larger than 69 502 cm^{-1} are to be used, change constant in register C to 143.88 and change 3 at step 95 to 2 to allow values up to 695 000 cm^{-1}. With this change, ε values are truncated beyond .01 cm^{-1}.

NOTE 3: If values for more than seventeen energy levels are inserted, the display will read Error. With seventeen levels, steps (3) and (5) each require 45 sec calculation time. With fewer levels, the time is cut as the calculation stops when a zero degeneracy is encountered. If calculations for a new atom or molecules is started by inserting new level values, one can start at step 2 if the same number or a greater number of levels is inserted: otherwise, one must reinsert the data card. If only the electronic contributions are desired, up to twenty levels can be stored if three pairs of fGSBO hRTN are added after step 36, RCLC at step 38 is replaced by 1438.8, RCLB at step 54 is replaced by 298.15, the 19 of steps 112-113 is changed to 22 after at least fifteen steps of the fLBLD subroutine have been deleted to accommodate the insertions.

cont'd.

Notes, cont'd.

NOTE 4: The dimensionless values for functions at 298 K given by steps (3) and (4) can be multiplied by R by the following procedure. After step (4), key R in the desired units followed by E to display $(H_{298}-H_o)_e$. Then R/S will display the electronic contributions to S_{298}, C_{298}, and $-(G_{298}-H_o)/T$. If the total $H^o_{298}-H^o_o$ is wanted for a gaseous atom, it can be obtained by adding 1481.20 to the electronic contribution in cal/mol.

NOTE 5: If $-(G-H_o)/RT$ is desired, it can be obtained after step 5 or any of the following steps by keying h RCI. Keying of g e^x would then give Q, the partition function.

Test with Si gas at 5000 K

(2)	1 ↑	0	A	0.010
	3 ↑	77.12	R/S	110960.030
	5 ↑	223.16	R/S	321082.050
	5 ↑	6298.86	R/S	9062799.050
	1 ↑	15394.37	R/S	22149419.01
	5 ↑	33326	R/S	47949448.05
	9 ↑	39860	R/S	57350568.09
	3 ↑	40992	R/S	58979289.03
	15 ↑	45303	R/S	65181956.15
	3 ↑	47284	R/S	68032219.03
	5 ↑	47352	R/S	68130057.05
	15 ↑	48161	R/S	69294046.15
	9 ↑	49128	R/S	70685366.09
	3 ↑	49400	R/S	71076720.03
	21 ↑	49966	R/S	71891080.21
	5 ↑	50189	R/S	72211933.05
	10 ↑	50535	R/S	72709758.10

(3) B 162.716

(4) R/S, 2.108, 0.176; 1.98719 E 323.347 R/S 4.190, 0.350, 3.105

(5) 5 EEX 3 C 2.279

(6') R/S 844.589, 2.448, 0.277, 2.279

(7) 1.98719 E 1678.4; (8) R/S 4.864, 0.550, 4.528

or after (5) (6"a) 28.086 D 12599.214; (6"b) R/S 27.579, 2.777, 25.059

(7) 1.98719 E 25037.031; (8) 54.804, 5.518, 49.796 cal.

Prgm. A

(2-1 to 3)	fLBLA	3	hSTI	hR↓	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	
(2-4 to 8)	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	
(2-9 to 13)	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN	
(2-14 to 16)	fGSB0	hRTN	fGSB0	hRTN	fGSB0	hRTN					36
(2-17)	fLBL0	RCLC	X	fINT	hx⇄y	EEX	2	÷	+	STO(i)	
	fISZ	hRTN	GTO9								49
(3)	fLBLB	fGSB1	0	STOE	RCLB	STOD	fGSB2	fGSB3	hR↑	STOE	
(4)	STOD	hRTN	RCL1	f-x-	RCL2	hRTN					65
(5)	fLBLC	STOD	fGSB1	fGSB2	GTO3						70
	fLBL1	0	STO0	STO1	STO2	3	hSTI	hRTN			78
	fLBL2	RCL(i)	↑	gFRAC	EEX	2	X	fx=0	hRTN	hx⇄y	
	fINT	EEX	3	÷	RCLD	÷	↑	hR↓	CHS	ge^x	
	X	STO+0	hR↑	X	STO+1	hSTx	X	STO+2	fISZ	1	
	9	hRCI	gx>y	hRTN	GTO2						113
	fLBL3	RCL2	RCL0	÷	RCL1	RCL0	÷	STO1	gx^2	-	
	STO2	RCL1	RCLD	X	RCLE	-	RCL0	fLN	hSTI	RCL1	
	+	STO1	RCLE	RCLD	÷	hRCI	+	STO0	hRTN		142
(6')	hR↑	STOD	CLX	RCL2	hx⇄y	gSTK	hRTN				149
($6''_a$)	fLBLD	hR↑	hx⇄y	fLN	hLSTx	RCLD	X	fLN	2	.	
	5	STO+2	STOC	X	hx⇄y	-	RCLA	-	↑	↑	
	hRCI	+	hSTI	hR↓	↑	↑	RCLC	+	STO+1	hR↓	
	RCLB	RCLD	÷	RCLC	X	+	STO+0	hR↓	RCLD	RCLB	
	-	RCLC	X	+	STOD	1	4	3	8	.	
($6''_b$)	8	STOC	hR↓	fLBL4	hRTN	RCL1	f-x-	RCL2	f-x-	RCL0	
	hRTN										210
(7,8)	fLBLE	STOX0	STOX1	STOX2	RCLD	X	STOD	GTO4			218

Data Tape: 3.665 STO A, 298.15 STO B, 1438.8 STO C.

R	0	1	2
	Q	Q'	Q''
	$\frac{-(G-H_{298})}{RT}$	Q'/Q	C/R
		S/R	

Registers 3 to 9 have $1438.8\varepsilon_i \cdot g_i \times 10^{-2}$ with i = 1 to 7

RS 0 to 9 have $1438.8\varepsilon_i \cdot g_i \times 10^{-2}$ with i = 8 to 17

R	A	B	C	D	E	I
	3.665	298.15	1438.8	T	$\frac{H_{298}-H_0}{R}$	3 to 20 several times $\frac{-(G-H_o)}{RT}$
			2.5	$\frac{H-H_{298}}{R}$		
			1438.8			

B. Calculation of Thermodynamic Functions from C_p or H Values

Heat capacity or enthalpy data may have been fit to $C_p/R = a+bT+cT^{-2}+dT^2$ or $C_p/R = a_0 + a_1T + a_2T^2 + a_3T^3$ using the programs of Chapter II. Programs CHSG and Cheb CHSG use the constants of these equations to calculate C_p/R, $(H-H_{298})/R$, S/R and $-(G-H_{298})/RT$.

The C_p equations generally will have a limited temperature range of application fixed by either the range of existence of the phase or by the range for which the equation gives a sufficiently accurate fit. Thus, the programs provide for joining at the temperature T_i at which a new range starts and $(H_i-H_{298})/R$ and S_i/R, calculated in the lower temperature range, are inserted to allow extension into the higher temperature range. The equations for Prgm. CHSG are based on $C_p/R = a + bT + cT^{-2} + dT^2$.

$$(H-H_i)/R = (T-T_i)[a+\tfrac{1}{2}b(T+T_i)+c/TT_i+\tfrac{1}{3}d(T^2+TT_i+T_i^2)]$$
$$(S-S_i)/R = a\ln(T/T_i) + (T-T_i)[b+\tfrac{1}{2}c(T+T_i)/T^2T_i^2+\tfrac{1}{2}d(T+T_i)]$$
$$-(G-H_{298})/RT = (S-S_i)/R + S_i/R - [(H-H_i)/R+(H_i-H_{298})/R]/T.$$

The constants a, b, c and d are stored in registers A, B, C and D. If the data have been fit to an equation with fewer constants, store 0 for the unused constants. The program has been illustrated with dimensionless functions; it operates equally well if the constants yield C_p rather than C_p/R. Then S_i and H_i-H_{298} should be inserted in steps 3 and 4 and the displays of steps 5 and 6 will be the indicated displays multiplied by R. If it is desired to convert the dimensionless displays of steps 5 and 6 to values in cal or j, R in the appropriate units should be stored in register E. Then step 7 will display the values multiplied by R. If the displays of steps 5-6 are already in dimensions, step 8 will divide by R from register E to display dimensionless values.

Directions

			Display
(1)	Insert Prgm. CHSG; store constants in registers A-D if not carried over from previous calculation		
(2)	T_i A		T_i
(3)	S_i/R SST		S_i/R
(4)	$(H_i-H_{298})/R$ SST; 0 SST if T_i = 298		$(H_i-H_{298})/R$
(5)	T B		C_p/R
(6)	SST SST SST		$(H-H_{298})/R$, S/R, $-(G-H_{298})/RT$
(7)	C to multiply by R		C_p, $H-H_{298}$, S, $-(G-H_{298})/T$
(8)	D to divide by R		

Prgm. CHSG

(2-4)	fLBLA	STO5	hRTN	STO4	STO3						
(5)	fLBLB	↑	STO2	RCL5	+	STO0	X	RCL5	gx^2	+	
	RCLD	X	3	÷	RCLC	RCL5	÷	RCL2	÷	+	
	RCL0	RCLB	X	2	÷	+	RCLA	+	RCL2	RCL5	
	-	STO1	X	RCL3	+	STO6	RCLC	2	÷	RCL0	
	X	RCL2	RCL5	X	gx^2	÷	RCLB	+	RCLD	2	
	÷	RCL0	X	+	RCL1	X	RCL2	RCL5	÷	fLN	
	RCLA	X	+	RCL4	+	STO7	hx⇄y	RCL2	÷	-	
	STO9	RCLD	RCL2	gx^2	X	RCLC	hLSTx	÷	+	RCLB	
(6)	RCL2	X	+	RCLA	+	STO8	hRTN	RCL6	RCL7	hR↑	
(7)	fLBLC	RCL9	RCLE	X	hSTI	RCL8	hLSTx	X	RCL6	hLSTx	
	X	RCL7	hLSTx	X	hRCI	gSTK	RTN				112
(8)	fLBLD	RCL9	RCLE	÷	hSTI	RCL8	hLSTx	÷	RCL6	hLSTx	
	÷	RCL7	hLSTx	÷	hRCI	gSTK	RTN				129

R	0	1	2	3	4	5	6	7	8	9
	$T+T_i$	$T-T_i$	T	$\frac{H_i-H_{298}}{R}$	$\frac{S_i}{R}$	T_i	$\frac{H-H_{298}}{R}$	$\frac{S}{R}$	$\frac{C_p}{R}$	$\frac{-(G-H_{298})}{RT}$

A	B	C	D	E	I
a	b	c	d	R	$\frac{-(G-H_{298})}{T}$

Test:

10 STO A, EEX CHS 3 STO B, 1 CHS EEX 5 STOC,

EEX CHS6 STOD, 1.98719 STOE

(2) 298.15 A; (3) 10 SST; (4) 0 SST

(5) EEX 3 B 11.900; (6) SST 7563, SST 22.747, SST 15.183;

(6) C 23.648, 15029, 45.202, 30.172

(7) D 5.888, 3806, 11.447, 7.641

From $C_p/R = a_0 + a_1T + a_2T^2 + a_3T^3$,

$$(H-H_i)/R = a_0(T-T_i) + \tfrac{1}{2}a_1(T^2-T_i^2) + \tfrac{1}{3}a_2(T^3-T_i^3) + \tfrac{1}{4}a_3(T^4-T_i^4)$$

$$(S-S_i)/R = a_0\ln(T/T_i) + a_1(T-T_i) + \tfrac{1}{2}a_2(T^2-T_i^2) + \tfrac{1}{3}a_3(T^3-T_i^3)$$

$$-(G-H_{298})/RT = (S-S_i)/R + S_i/R - [(H-H_i)/R + (H_i-H_{298})/R)]/T$$

a_0 to a_3 will be in R6 to R9 if evaluated by Prgm. Cheb-a.

Directions:

(1) Insert Prgm. Cheb CHSG and a_0 to a_3 in R6-8 if not already there

		Display
(2)	T_i A	T_i^2
(3)	S_i/R SST	S_i/R
(4')	$(H_i-H_{298})/R$ SST	$(H_i-H_{298})/R$
(4")	R SST	R
(5)	T B	C_p/R
(6)	SST SST SST	$(H-H_{298})/R$, S/R, $-(G-H_{298})/RT$

(7) C repeats display of steps 5 & 6 multiplied by R if R has been stored in register E by step 4".

(8) D repeats display of steps 5 & 6 divided by R if the a_n constants gave C_p in dimensions of R and therefore steps 5 & 6 gave the indicated quantities multiplied by R.

NOTE: After step 6, another SST will flash in turn the four values previously displayed if a review is wanted.

Prgm. Cheb CHSG

(2-4)	fLBLA	STOA	gx^2	STOB	hRTN	STOC	STOD	STOE			8
(5)	fLBLB	hSTI	RCLA	−	STO5	RCL6	X	hRCI	gx^2	RCLB	
	−	STO4	RCL7	X	2	÷	+	hRCI	3	hy^x	
	RCLA	RCLB	X	−	STO3	RCL8	X	3	÷	+	
	hRCI	4	hy^x	RCLB	gx^2	−	RCL9	X	4	÷	
	+	RCLD	+	STO1	hRCI	÷	RCL3	RCL9	X	3	
	÷	RCL4	RCL8	X	2	÷	+	RCL5	RCL7	X	
	+	hRCI	RCLA	÷	fLN	RCL6	X	+	RCLC	+	
	STO2	hx⇄y	−	STO3	RCL9	hRCI	X	RCL8	+	hRCI	
	X	RCL7	+	hRCI	X	RCL6	+	STO0	hRTN	RCL1	
(6)	RCL2	hR↑	gSTK								101
(7)	fLBLC	RCL3	RCLE	X	STO4	RCL0	RCLE	X	RCL1	RCLE	
	X	RCL2	RCLE	X	RCL4	gSTK	hRTN				118
(8)	fLBLD	RCL3	RCLE	÷	STO4	RCL0	RCLE	÷	RCL1	RCLE	
	÷	RCL2	RCLE	÷	RCL4	gSTK	hRTN				135

R	0	1	2	3	4	5	6	7	8	9
				$T^3-T_i^3$	$T^2-T_i^2$	$T-T_i$	a_0	a_1	a_2	a_3
	C_p/R	$(H-H_{298})/R$	S/R	$-(G-H_{298})/RT$	$-(G-H_{298})/T$					

R	A	B	C	D	E	I
	T_i	T_i^2	S_i/R	$(H_i-H_{298})/R$	R	T

Test:

$C_p = a_0 + a_1T + a_2T^2 + a_3T^3$ with Prgm. CHSG

1.50365 STO 6, 8.19918×10^{-3} STO 7, -4.13509×10^{-6} STO 8, 9.21717×10^{-10} STO 9;

(2) 1400 A; (3) S_{1400} = 16.792 cal K^{-1} SST; (4) $H_{1400}-H_{298}$ = 7307 cal SST, 1.98719 SST; (5) 1400 B 7.407, SST 7307, SST 16.792, SST 11.573; 2800 B 12.276, SST 20 320, SST 23.057, SST 15.800; SST reviews the four values, D divides them by R.

The programs of Chapters I and II have provided least-square fits of enthalpy or heat capacity data to four constant equations. Programs CHSG and Cheb CHSG calculate values of the other thermodynamic functions from the four constant heat capacity equations. Using eight values of the C_p of molybdenum solid at 200 K intervals from 1400 to 2800 K,

$$C_p = 1.5037 + 8.1992\times10^{-3}T - 4.1351\times10^{-6}T^2 + 9.2172\ 10^{-10}T^3$$

was obtained which fit the original values with an average deviation of 0.009 or less than 0.1%. The same values were fit by Prgm. LS C_p^*, which uses only three independent constants, to obtain

$$C_p = 9.5466 - 3.8026\times10^{-3}T - 1.360\times10^{5}T^{-2} + 1.6987\times10^{-6}T^2.$$

This equation fits the original values with an average deviation of 0.06 or about 0.6%. Both equations were used with Prgms. Cheb CHSG and CHSG, res-respectively. The values of $-(G-H_{298})/T$ calculated by Prgm. CHSG using the constants from Prgm. LS C_p^* were only slightly lower than those calculated using the constants from Prgm. Cheb-a with an average deviation of 0.002 or 0.02%, thus illustrating the insensitivity of $(G-H_{298})/T$ values to errors in C_p.

It is sometimes useful to go directly from the analytical equations for C_p to an analytical equation for $-(G-H_{298})/T$, which will have six terms derived from the four terms of the original heat capacity equations. Prgm. CgK described below carries out this operation. This program not only calculates values of $-(G-H_{298})/T$, but if the constants for each of the reactants and products of a reaction are combined to obtain an equation for ΔC_p^o, the program calculates $-(\Delta G^o-\Delta H_{298}^o)/T$ for a given T. The program can be used for either C_p^o or C_p^o/R. The program provides for multiplication or division by R to provide consistency.

The ability to calculate $-(\Delta G^\circ - H^\circ_{298})/RT$ allows calculation of $\Delta H^\circ_{298}/R$ from a value of K, the equilibrium constant, or the calculation of K from knowledge of $\Delta H^\circ_{298}/R$. Normally the C_p equations will be of the same form and $\Delta C_p/R$ will either be

$$\Delta a_0 + \Delta a_1 T + \Delta a_2 T^2 + \Delta a_3 T^3 \quad \text{or} \quad \Delta a + \Delta bT + \Delta cT^{-2} + \Delta dT^2.$$

Prgm. CgK will handle either form. In addition, if not all of the reactants or product heat capacities are in the same form, the program will handle $\Delta C_p/R = \Delta a_0 + \Delta a_1 T + \Delta a_2 T^2 + \Delta a_3 T^3 + \Delta cT^{-2}$. Constants of terms that are not used should be entered as zero.

$\Delta C^\circ_p/R = \Delta cT^{-2} + \Delta a_0 + \Delta a_1 T + \Delta a_2 T^2 + \Delta a_3 T^3$ where b terms are included in Δa_1 and d terms are included in Δa_2.

$-(\Delta G^\circ - \Delta H^\circ_{298})/RT = \Delta a_0 \ln T + \Delta a_{-2} T^{-2} + \Delta a_{-1} T^{-1} + \Delta a'_0 + \Delta a'_1 T + \Delta a'_2 T^2 + \Delta a'_3 T^3$

where $\Delta a'_3 = \frac{1}{12}\Delta a_3$, $\Delta a'_2 = \frac{1}{6}\Delta a_2$, $\Delta a'_1 = \frac{1}{2}\Delta a_1$, $\Delta a_{-2} = \frac{1}{2}\Delta c$,

$\Delta a'_0 = \Delta S^\circ_i/R - \Delta a_0(\ln T_i + 1) + \frac{1}{2}\Delta cT_i^{-2} - \Delta a_1 T_i - \frac{1}{2}\Delta a_2 T_i^2 - \frac{1}{3}\Delta a_3 T_i^3$, and

$\Delta a_{-1} = \Delta a_0 T_i + \frac{1}{2}\Delta a_1 T_i^2 + \frac{1}{3}\Delta a_2 T_i^3 + \frac{1}{4}\Delta a_3 T_i^4 - \Delta cT_i^{-1} - (\Delta H^\circ_i - \Delta H^\circ_{298})/R$.

The equations are written for ΔH°_{298} but can be used for ΔH°_o and $(\Delta G - \Delta H_o)/RT$ if $(\Delta H^\circ_i - \Delta H^\circ_{298})/R$ is replaced by $(\Delta H^\circ_i - H^\circ_o)/R$. T_i is the temperature limit for range of validity of the C_p equations. The following equations are used for calculation of K, $\Delta H^\circ_{298}/R$, or $\Delta G^\circ/R$.

$$\Delta H^\circ_{298}/R = T[-(\Delta G^\circ - \Delta H^\circ_{298})/RT - \ln K].$$

The values of ΔH°_{298} from a set of T and K values are averaged and then used for calculation of $\Delta G^\circ/R$ and K by $\ln K = -\Delta G^\circ/RT = -(\Delta G^\circ - H^\circ_{298})/RT - (\Delta H^\circ_{298}/R)T^{-1}$.

When accurate entropies are not available for all reactants and products, both ΔH° and ΔS° can be determined[21] through evaluation of

$$\Delta H^\circ_{298}/R - T\Delta S^\circ_i/R = T[-(\Delta G^\circ - H^\circ_{298})/RT - \Delta S^\circ_i/R - \ln K] = T[A - \ln K]$$

where A can be calculated from just the constants of the $\Delta C^\circ_p/R$ equations by step 10 of Prgm. CgK if zero is entered for $\Delta S^\circ_i/R$ in step 3. If steps 14 and 15 are carried out for a set of T and K values with $\Delta S^\circ_i/R = 0$, the display of step 15 is $\Delta H^\circ_{298}/R - T\Delta S^\circ_i/R$ which is stored in the secondary register. These values can then be least-square fit to a linear equation after all data have been inserted in steps 14 and 15 by carrying out step 21. Step 21 displays first $\Delta H^\circ_{298}/R$ followed by $\Delta S^\circ_i/R$ and incorporates these constants; so that steps 10 and 18 to 20 can then be carried out.

Directions:

(1) Insert Prgm. CgK

(2) Store Δa_0 in R0, Δa_1 in R1, Δa_2 in R2, Δa_3 in R3, Δc in RC, and R = 1.98719 or 8.3144 in RE.

		Display
(3)	$T_i \uparrow \Delta S_i^\circ/R \uparrow (\Delta H_i^\circ - \Delta H_{298}^\circ)/R$ A	Δa_0
(4)	SST	Δa_{-2}
(5)	SST	Δa_{-1}
(6)	SST	$\Delta a_0'$
(7)	SST	$\Delta a_1'$
(8)	SST	$\Delta a_2'$
(9)	SST	$\Delta a_3'$
(10)	T B	$-(\Delta G^\circ - \Delta H_{298}^\circ)/RT$
(11)	f a to multiply by R	
(12)	f e to divide by R	
(13)	f c before starting set of data in steps 14 and 15	0.00
(14)	$T_i \uparrow K_i$ C repeat for all i	$\Delta H_{298}^\circ/R$
(16)	R/S	$\frac{1}{i}\Sigma\Delta H_{298}^\circ/R$
(17)	R/S	Standard Deviation
(18)	T D	K
(19)	SST	ln K
(20)	T E	$\Delta G^\circ/R$
(21)	f d after step 15 if $\Delta S_i^\circ/R = 0$ in step 3	$\Delta H_{298}^\circ/R$, $\Delta S_i^\circ/R$

NOTE 1: Enter 0 for $(\Delta H_i^\circ - \Delta H_{298}^\circ)/R$ if T_i = 298.15 K and enter zero for Δc, Δa_3, or Δa_2 if the C_p equations do not use these terms.

NOTE 2: If it is desired to repeat the calculations using a changed value of T_i, it is necessary to start back at step 2. Steps 4 to 9 can be bypassed if there is no need to check the constants. With $\Delta S_i^\circ/R$ known and stored in RA and step 3 completed, steps 10-12, 18 and 20 can be carried out in any order. If S_i°/R is known and has been inserted in step 3, steps 16 and 17 follow the insertion of all of the sets of K and T values. If S_i°/R is not known, it is entered as zero in step 3 and steps 10 and 16-20 cannot be used until $\Delta S_i^\circ/R$ has been determined by carrying out step 21 after the insertion of all of the sets of K and T values. After step 21, steps 10, 18 and 20 can be used in any order.

Prgm. CgK

(3)	fLBLA	STOB	hR↓	STOA	hR↓	↑	↑	STOD	RCL3	4	
	÷	X	RCL2	3	÷	+	X	RCL1	2	÷	
	+	X	RCL0	+	X	RCLC	hR↑	÷	−	RCLB	
	−	STO4	hR↓	RCL3	3	÷	X	RCL2	2	÷	
	+	X	RCL1	+	X	RCLC	hR↑	gx^2	÷	2	
	÷	−	hR↑	fLN	1	+	RCL0	X	+	RCLA	
	−	CHS	STO5	2	STO÷1	6	STO÷2	1	2	STO÷3	
(4-7)	RCLC	2	÷	STOC	RCL0	hRTN	RCLC	RCL4	RCL5	RCL1	
(8-9)	RCL2	RCL3									82
(10)	fLBLB	↑	↑	↑	RCL3	X	RCL2	+	X	RCL1	
	+	X	RCL4	hR↑	÷	+	RCLC	hR↑	gx^2	÷	
	+	RCL5	+	hR↑	fLN	RCL0	X	+	hRTN		111
(11)	gLBLa	RCLE	X	hRTN							115
(12)	gLBLe	RCLE	÷	hRTN							119
(13)	gLBLc	fP≠S	0	STO4	STO5	STO6	STO7	STO8	STO9	fP≠S	
(14)	hRTN	fLBLC	fLN	STO6	hR↓						134
(16)	B	RCL6	−	X	hR↑	Σ+	hR↓	hRTN	$f\bar{x}$	hR↓	149
(17)	STO7	hRTN	gs	hR↓	hRTN						
(18-19)	fLBLD	B	RCL7	hR↑	÷	−	ge^x	hRTN	fLN		158
(20)	fLBLE	B	X	CHS	RCL7	+	hRTN				165
(21)	gLBLd	fP≠S	RCL4	RCL6	X	RCL9	RCL8	X	−	RCL4	
	gx^2	RCL9	RCL5	X	−	÷	CHS	STOA	RCL4	X	
	RCL6	+	RCL9	÷	fP≠S	STO7	f-x-	RCLA	STO+5	hRTN	195

RP	0	1	2	3	4	5	6	7
	Δa_0	Δa_1	Δa_2	Δa_3				
		$\Delta a'_1$	$\Delta a'_2$	$\Delta a'_3$	Δa_{-1}	$\Delta a'_0$	lnK	$\frac{1}{i}\Sigma\Delta H^\circ_{298}/R$

RS	4	5	6	7	8	9
	ΣT	ΣT^2	$\Sigma\Delta H^\circ_{298}/R$ or $\Sigma\frac{\Delta H^\circ_{298}-T\Delta S^\circ_i}{R}$	$\Sigma(\Delta H^\circ_{298}/R)^2$	$\Sigma T(\Delta H^\circ_{298}/R)$	i

R	A	B	C	D	E
	$\Delta S^\circ_i/R$	$\frac{\Delta H^\circ_i-\Delta H^\circ_{298}}{R}$	Δc	T_i	R
			Δa_{-2}		

Test with $C_p = a_0 + a_1T + a_2T^2 + a_3T^3$ for Mo, 1400-2800 K:

(2) 1.50365 STO 0, 8.19918×10^{-3} STO 1, -4.13509×10^{-6} STO 2, 9.21717×10^{-10} STO 3, 0 STO C, 1.98719 STO E;

(3) 1400 ↑ 16.792 ↑ 7307 A 1.50365; (4) SST 0; (5) SST -63.706;

(6) SST -3.874; (7) SST 4.0996×10^{-3}; (8) SST -6.892×10^{-7}; (9) SST 7.681×10^{-11};

(10) 1400 B 11.573; (12) f e 5.824; (10) 1800 B 12.956;

(10) 2200 B 14.171; (10) 2800 B 15.800; (12) f e 7.951; (11) f a 15.800.

Test with $C_p = a + bT + dT^2 + cT^{-2}$ for Mo, 1400-2800 K

(2) 9.54656 STO 0, -3.80258×10^{-3} STO 1, 1.6987×10^{-6} STO 2, 0 STO 3, -1.35954×10^{5} STO C, 1.98719 STO E;

(3) 1400 ↑ 16.792 ↑ 7307 A 9.54656; (4) SST -67 977; (5) SST 3982.51;

(6) SST -58.2878; (7) SST -1.90129×10^{-3}; (8) SST 2.8312×10^{-7}; (9) SST 0;

(10) 1400 B 11.573; (12) f e 5824; (10) 1800 B 12.955;

(10) 2200 B 14.168; (10) 2800 B 15.796; (12) f e 7.949; f a 15.796

Test of complete program with ΔS_i^o known

(2) 1 STO 0, 10^{-3} STO 1, 10^{-6} STO 2, 0 STO 3, -10^{6} STO C, 1.98719 STO E;

(3) 10^3 ↑ 20 ↑ 100 A 1.000; (4) SST -5×10^{5}; (5) SST 2733 $\frac{1}{3}$; (6) SST 10.092;

(7) SST 5×10^{-4}; (8) SST $\frac{5}{3}\times10^{-7}$; (9) 0; (10) 10^3 B 19.900;

(10) 2000 B 20.601; (11) f a 40.939; (12) f e 20.601 (13) f c 0.000;

(14) 10^3 ↑ 0.905 C 19 999.8; (14) 2×10^3 ↑ 40 194 C 2000.0;

(16) R/S 19 999.9; (17) R/S 0.3; (18) 10^3 D 0.905;

(19) SST -0.100 (18) 2000 D 40 196; (19) SST 10.602; (20) 10^3 E 99.918

Test of program with ΔS_i^o to be determined

(2) same as above; (3) 10^3 ↑ 0 ↑ 100 A 1.00; (4&5) same as above;

(6) SST -9.908, (7-9) same as above; (13) f c 0.000;

(14) 10^3 ↑ 0.905 C -0.180; (14) 2×10^3 ↑ 40194 C -19 999.98;

(21) f d 19 999.6, 20.00; (10) 10^3 B 19.900; (10) 2000 B 20.601

As Prgm. CgK would be repeatedly used for equilibrium calculations of the solidus-liquidus equilbria for molybdenum, it is worthwhile to use a variant of Prgm. CgK specifically designed for this type of equilibrium calculation. The program can be simplified by calculating $-(\Delta G^{o}-\Delta H^{o}_{Std})/RT$ for the fusion process at several evenly spaced temperatures and fitting these values with Prgms. Cheb (f,C_n) and Cheb-a. The resulting four a_n values are then put on a data tape to be stored in registers 0 to 3. Also $\Delta H^{o}_{Std}/R$ for the fusion process would be on the tape to be stored in register 9. The atomic weight of molybdenum, 95.94 would be stored in register C to be used if any data in weight percent are to be converted to mole fraction. With the molefractions of Mo in the solid and liquid phases at a given temperature, the program provides values of γ_L/γ_S and $\ln\gamma_L/x_2^2$. For values at several temperatures, a least-square fit is made to estimate the excess entropy and enthalpy of mixing in the liquid phase. With these constants and for systems with moderate solid solubilities, the liquidus curve can then be calculated by the present program.

The choice of standard temperature to serve as a reference for enthalpy values and the choice of liquid standard state is sometimes found to be confusing. A number of possible choices for molybdenum were discussed in detail in Ref.(13) to demonstrate that the final calculations do not depend upon the arbitrary choices that can be made. A summary of the different types of calculations from Ref.(13) is presented here. The heat capacity data for Mo(s) at 200 K intervals from 1400 to 2800 K were fit by Prgms. Cheb (f,C_n) and Cheb-a. The heat capacity of Mo(l) was extrapolated to lower temperatures by $C_p^{o}/R = 2.832 + 5.923\times10^{-4}T$ to join the solid C_p^{o} at 800 K. For Mo(s) = Mo(l), $\Delta C_p^{o}/R = 2.075 - 3.534\times10^{-3}T + 2.0809\times10^{-6}T^2 - 4.638\times10^{-10}T^3$ for 1400-2800 K. This choice of C_p for Mo(l) fixes the metastable liquid standard state between 1400 and the melting point. If 298.15 K is chosen as the reference temperature and ΔH^{o}_{Std} is the enthalpy of fusion at 298 K, the method of extrapolating the liquid thermodynamic properties from 1400 K to 298 K can be completely arbitrary with no effect upon the calculations in the operating range of 1400 to 2890 K. This is most simply seen from the equation

$$\ln K = -\Delta G^{o}/RT = -(\Delta G^{o}-\Delta H^{o}_{Std})/RT - \Delta H^{o}_{Std}/RT = \emptyset - (\Delta H^{o}_{i}-\Delta H^{o}_{Std})/RT-\Delta H^{o}_{Std}/RT$$

where $\emptyset$ represents those terms of $-(\Delta G^\circ - \Delta H^\circ_{Std})/RT$ that depend only upon the heat capacity contributions and T_i, the bound to the range of validity of the heat capacity equation, and not upon T_{Std}. It is apparent that any change in the standard reference temperature or in the methods of extrapolating to the standard reference temperature cancels out due to an equal change in $(\Delta G - \Delta H^\circ_{Std})/RT$ and in $\Delta H^\circ_{Std}/RT$. This was illustrated in Ref.(13) by using different heat capacity equations for liquid Mo between 298 and 1400 K and as expected from the above equation, identical values of ln K are obtained in the range 1400-2890 K. Also the use of 2890 K instead of 298 K as the standard reference temperature gave identical ln K values. Likewise, T_{Std} = 0 K changes $(\Delta H^\circ_i - \Delta H^\circ_{Std})/RT$ and $\Delta H^\circ_{Std}/RT$ equally. If the same standard reference state, e.g. Mo(s) at 298.15 K, is used for both the solid and liquid phases such that $\Delta H^\circ_{298} = 0$ for Mo(s) = Mo(l), $\Delta H^\circ_{1400} - \Delta H^\circ_{Std}$ is changed correspondingly to yield the same $\Delta G^\circ/RT$. The various quantities are shown for comparison where A corresponds to extrapolation of the liquid C_p equation from 1400 to 298 K; B takes $\Delta C_p = 0$ from 800 to 298 K, C refers both liquid and solid to the solid reference state at 298 K and D uses 2890 K as the standard reference temperature.

	A	B	C	D
T_{Std}	298.15	298.15	298.15	2890 K
$\Delta H^\circ_{Std}/R$	5305	5323	0	4303 K
$(\Delta H^\circ_{1400} - \Delta H^\circ_{Std})/R$	2	17	5307	1005 K
$-(\Delta G^\circ_{1400} - \Delta H^\circ_{Std})/RT$	1.904	1.916	-1.885	1.188
$-\Delta G^\circ_{1400}/RT$	-1.886	-1.886	-1.886	-1.885

Within the limit of rounding errors, the final results are identical.

Since there is no difference, Prgm. Ωxb is set-up to use the conventional standard reference temperature of 298.15 K but a wider temperature range is handled than previously (13). For the range 900 K to the melting point, $C^\circ_p/R = 2.18 + 2.0484\times10^{-3}T - 1.1049\times10^{-6}T^2 + 0.31558\times10^{-9}T^3$ was used for the solid. For the liquid, $C^\circ_p/R = 2.832 + 5.923\times10^{-4}T$ was used to extrapolate from the value of 4.544 at 2890 K to join the solid value of 3.306 at 800 K. For Mo(s) = Mo(l), $\Delta C^\circ_p/R = 0.651 - 1.456\times10^{-3}T + 1.1049\times10^{-6}T^2 - 0.31558\ 10^{-9}T^3$ from 900 K to the melting point. ΔC°_p was taken as

zero below 900 K. $\Delta H^{\circ}_{2890}/R = 4303$, $\Delta H^{\circ}_{900}/R = \Delta H^{\circ}_{298}/R = 5329$ K and $\Delta S^{\circ}_{900}/R = -(\Delta G^{\circ}_{900}-\Delta H^{\circ}_{298})/RT = 1.921$.

The constants of the ΔC°_{p} equation were inserted in Prgm. CgK with $T_i = 900$, $\Delta S^{\circ}_{i}/R = 1.921$, and $(\Delta H^{\circ}_{i}-\Delta H^{\circ}_{298})/R = 0$. Values of $-(\Delta G^{\circ}-\Delta H^{\circ}_{298})/RT$ were calculated ranging from 900 K to the melting point and fitted with Prgms. Cheb. C_n-(f,C_n) and Cheb-a_3 to obtain

$$-(\Delta G^{\circ}-\Delta H^{\circ}_{298})/RT = 1.9357 - 3.544\times10^{-5}T + 3.123\times10^{-8}T^2 - 1.042\times10^{-11}T^3$$

for Mo(s) = Mo(l) between 900 K and the melting point with an average deviation of less than 0.001 compared to the values from Prgm. CgK.

$K = x^{L}_{Mo}\gamma^{L}_{Mo}/x^{S}_{Mo}\gamma^{S}_{Mo}$ and $\gamma^{L}_{Mo}/\gamma^{S}_{Mo}$ are calculated from the equation

$$\ln K = -\Delta G^{\circ}/RT = -(\Delta G^{\circ}-\Delta H^{\circ}_{298})/RT - \Delta H^{\circ}_{298}/RT = \ln\gamma^{L}_{Mo}/\gamma^{S}_{Mo} + \ln x^{L}_{Mo}/x^{S}_{Mo}.$$

From just the liquidus curve, it is not possible to unambigously fix the enthalpy of mixing and the excess entropy of mixing for the solution. However, the approximation of assuming that both the enthalpy of mixing and the excess entropy of mixing vary as $(1-x_{Mo})^2$ is made for preliminary treatment of the data. $\Delta\bar{H}_{Mo}/R = b_h(1-x^{L}_{Mo})^2$, $\Delta\bar{S}^{E}_{Mo}/R = +b_s(1-x^{L}_{Mo})^2$, and $\ln\gamma^{L}_{Mo} = \Delta\bar{G}^{E}_{Mo}/RT = (b_h/T - b_s)(1 - x^{L}_{Mo})^2$ where the partial molal quantities are for the mixing of liquid Mo with the other component. At a given temperature, $b_h/T - b_s$ will be designated as Ω. When x^{S}_{Mo} and γ^{S}_{Mo} are close to unity, $\ln\gamma^{S}_{Mo}$ will be very small and will be approximated by $\ln\gamma^{S}_{Mo} = [\ln(\gamma^{L}_{Mo}/\gamma^{S}_{Mo})](1-x^{S}_{Mo})^2/(1-x^{L}_{Mo})^2$. If the resulting $\gamma^{S}_{Mo}x^{S}_{Mo} > 1$, γ^{S}_{Mo} is approximated by $\frac{1}{x^{S}_{Mo}}$. Then multiplication of $\gamma^{L}_{Mo}/\gamma^{S}_{Mo}$, determined in the equation above from the liquidus and solidus points and $\Delta G^{\circ}/RT$ of fusion, by γ^{S}_{Mo} will yield γ^{L}_{Mo} which can then be converted to Ω or $b_h/T - b_s$. From values at several temperatures, a least square fit will yield the values of b_h and b_s from which the first approximation to the enthalpy and excess entropy of mixing of liquid Mo with the other component will be available. Then using bonding theory to fix reasonable enthalpy and entropy values, a second approximation to b_h and b_s is obtained that fits both the liquidus data and provides reasonable enthalpy and entropy values. An approximate liquidus curve can be calculated using the initial b_h and b_s with an estimated solid solubility. The program also provides for converting Celsius temperatures to Kelvin and converting weight percent to molefraction.

Directions:

		Display
(1)	Insert Prgm. Ωxb	
(2)	Insert data tape with constants of equation for $-(\Delta G^o-\Delta H^o_{298})/RT$ and ΔH^o_{298} for the fusion of Mo and the atomic weight of Mo.	
(3)	If any weight percent data are to be treated, store atomic weight of second component in register C.	
(4)	E (to preceed each new set of data)	0.000
(5)	T ↑ $(1-x^S_{Mo})$ ↑ $(1-x^L_{Mo})$ A	Ω, $\gamma^L_{Mo}/\gamma^S_{Mo}$
	Repeat step 5 for data at each T	
(6)	R/S after all data entered in step 5	b_h, b_s
(7)	$(1-x^S_{Mo})$↑$(1-x^L_{Mo})$B	values will flash until T within 2°
(8)	T f a	$-\Delta G^o_f/RT$
(9)	t C	T
(10)	wt.%A D	$x_A = (1-x_{Mo})$

NOTE 1: Step 9 is used to preceed steps 5, 7 and 8 when t°C is to be converted to T°K.

NOTE 2: Step 5 calls for $x_A = (1-x_{Mo})$. When wt.%A is available, step (10) converts to x_A. Starting with wt.%Mo, key 100 wt.%Mo - D for step 5.

NOTE 3: The initiation of a new set of data in step 5 must be initiated by step 4 which clears the secondary registers. At any time after completion of step 5 and before step 4 is carried out to prepare for a new set of data, step 6 can be repeated by keying f c.

NOTE 4: In step 7, small values of x^S_A have little effect on the liquidus and a rough estimate can be used. $x^S_A=10^{-4}$ or 10^{-5} can be used for all very small solid solubilities. The calculation is inadequate for large solid solubilities.

NOTE 5: The values of b_h and b_s obtained in step (6) are sensitive to experimental error. After modification to match reasonable enthalpies and excess entropies, the revised b_h is stored in R5 and the revised b_s is stored in RI; step 7 will then use these values for calculation of the liquidus curve.

NOTE 6: To use for another component, store $\Delta H^o_f/R$ in A, $\Delta S^o_f/R$ in 0, and 0 in 1-3 if $\Delta C_p = 0$. In steps 5 and 7, x_{Mo} is replaced by x_2. When $\Delta C_p \neq 0$, the next level of approximation is to use the average values of $\Delta H^o_f/R$ and $\Delta S^o_f/R$ over the temperature range. For Mo, one can use $\Delta H^o_f/R = 5127$ and $\Delta S^o_f/R = 1.774$ as averages for 1400-2890 K.

Prgm. Ωxb

(9)	fLBLC	RCLD	+	hRTN							4
(10)	fLBLD	EEX	2	:	hl/x	1	−	RCLC	X	RCLB	
	:	1	+	hl/x	hRTN						19
(4)	fLBLE	fP⇄S	0	STO4	STO5	STO6	STO8	STO9	fP⇄S	hRTN	
(5)	fLBLA	STOE	1	−	hx⇄y	hSTI	1	−	÷	fLN	
	STO6	hR↓	STO4	fa	RCL6	−	STO9	hRCI	RCLE	÷	
	gx^2	X	↑	↑	1	hRCI	−	fLN	+	fx>0	
	fGSB1	hR↓	STO8	RCL9	+	RCLE	gx^2	÷	STO7	RCL4	
	X	hLSTx	Σ+	hLSTx	÷	f-x-	RCL9	ge^x	hRTN		78
(6)	gLBLfc	fP⇄S	RCL4	RCL6	X	RCL8	RCL9	X	−	RCL4	
	gx^2	RCL9	RCL5	X	−	÷	CHS	hSTI	RCL4	X	
	RCL6	+	RCL9	÷	fP⇄S	STO5	f-x-	hRCI	hRTN		107
(7)	fLBLB	1	STO8	STO9	hR↓	STO-9	gx^2	hx⇄y	STO-8	gx^2	
	−	↑	↑	RCL5	X	RCLA	+	STO7	RCL8	RCL9	
	÷	fLN	hR↑	hRCI	X	+	STO6	RCL0	+	÷	
	fLBL3	f-x-	fa	RCLA	hR↑	÷	+	RCL7	hx⇄y	RCL6	
	+	÷	STO4	−	hABS	2	gx≤y	GTO4	RCL4	hRTN	
	fLBL4	RCL4	GTO3								160
(8)	gLBLfa	↑	↑	↑	RCL3	X	RCL2	+	X	RCL1	
	+	X	RCL0	+	RCLA	hR↑	÷	−	hRTN		179
	fLBL1	1	hRCI	−	fLN	CHS	↑	hRTN			187

RP	0	1	2	3	4	5	6	7	8	9
	a_0	a_1	a_2	a_3	T	b_h	$\ln \frac{x^L_{Mo}}{x^S_{Mo}}$	Ω	$\ln \gamma^S_{Mo}$	$\ln \frac{\gamma^L_{Mo}}{\gamma^S_{Mo}}$
							used	used	x^S_{Mo}	x^L_{Mo}

RS	4	5	6	7	8	9
	ΣT	$ΣT^2$	ΣΩT	$ΣΩ^2T^2$	$ΣΩT^2$	i

R	A	B	C	D	E	I
	$ΔH^o_{298}/R$	95.94	M_A	273.15	x^L_A	x^S_A
						b_s

Test:

(3) 157.26 STO C

(9) 150 C 423.15; (10) .09 D 5.49×10^{-4}, 1.53 D 9.39×10^{-3};

(4) E 0.000; (5) 2800 ↑ 10^{-3} ↑ .0553 A 1.715, 1.005;

(5) 2700 ↑ 10^{-4} ↑ .132 A 1.741, 1.031; (5) 2600 ↑ 10^{-5} ↑ .2522 A 1.769, 1.119;

(5) 2500 ↑ 10^{-6} ↑ .54202 A 1.800, 1.697; (5) 2400 ↑ 10^{-6} ↑ .7315 A 1.833, 2.667;

(6) R/S 1977.8, -1.009; (7) 10^{-3} ↑ .0553 B 2683, 2783, 2797,2800,2800;

(7) 10^{-5} ↑ .2522 B 2523, 2592,2599,2600; (8) 2700 f a -0.111;

(6) f c 1977.8, -1.009

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[12,20] 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.[12] 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, $b_g T$ at a temperature T equals $b_h - b_s T$, 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. 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 ↑ T_2 ÷ STO X 4 RCL 4 f b 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(18). 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 DSP 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 DSP 4. If it is desired to calculate x and y more accurately, steps 7 and 6 can be repeated with DSP 3 or 4. If there is no interest in the progress of the iteration at each step, hCFO will stop the flashing of successive x or y values. hSFO 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 $e_x = \Delta G^o_{f,1}/RT = \Delta H^o_{f,1}/RT - \Delta S^o_{f,1}/R$ and $e_y = -\Delta G^o_{f,2}/RT = -\Delta H^o_{f,2}/RT + \Delta S^o_{f,2}/R$, where ΔH^o_f and ΔS^o_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, $\Delta H^o_{f,1}$, $\Delta S^o_{f,1}$, $\Delta H^o_{f,2}$ and $\Delta S^o_{f,2}$ are entered as zero. When the difference in standard states corresponds to the solid phase transition, then ΔH^o_f and

ΔS_f^o 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)	DSP n, usually n=2 initially	
(3)	$\Delta H_{f,1}^o/R \uparrow \Delta S_{f,1}^o/R \uparrow b_h^x \uparrow b_s^x$ A	$\Delta H_{f,1}^o/R$
(4)	$-\Delta H_{f,2}^o/R \uparrow -\Delta S_{f,2}^o/R \uparrow b_h^y \uparrow b_s^y$ R/S (or fa)	$-\Delta H_{f,2}^o/R$
(5)	$c_h^y \uparrow c_s^y \uparrow c_h^x \uparrow c_s^x$ R/S (or fb)	c_h^y
(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 DSP n+1	x" ..... x'''
(8)	R/S	y" ..... y'''

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

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

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

(7")	x STO A fd	d_y
(8")	C	y" ..... y_{final}

NOTE 1: The alternatives fa and fb 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 3 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 fP≥S before starting again at step 6.

cont'd.

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 DSP n and repeat steps 8' and 7'. Similarily, if x is known, repeat steps 7" and 8".

NOTE 5: After T STOD, E calculates $\Delta G^{o}_{f,1}/RT$, GTO 6 R/S calculates b_x and fc calculates c_x for component 1 if the component 1 constants are in the primary registers. If $d_x = -\ln a_1$ is desired, it may be obtained by RCL5 after step 8.

NOTE 6: Step 6 assumes x and y are small. If they are not, replace step 6 by T STO D x' ↑ y' GTO 8 R/S, where x' and y' are estimates of the solution. Then continue with steps 7 and 8. This procedure is also used for calculating solubilities for a sequences of temperatures. If the temperature intervals are small, only T STOD is needed for step 6.

TEST:

(3) 5127 ↑ 1.774 ↑ 4×10^3 ↑ .3 A 5127.00;

(4) -1371 ↑ -.762 ↑ 8×10^3 ↑ .2 R/S -1371.00;

(5) 500 ↑ .1 ↑ 500 ↑ .1 R/S 500.00;

(6) 2×10^3 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, DSP 4, .0190;

(7) C x=.1014, .1014,.1014,.1014, DSP 5, .10138;

(8) R/S y=.01902, .01902,.01902, DSP 6, .019022.

y = .019022 known

Steps 2-7 the same as above; (8') .019022 STO A fd, d_x=.0177;

(7') C .1014, .1014, .1014, DSP 5, .10138

x = .10138 known

Steps 2-6 the same as above; (7") .10138 STO A fd, d_y = .0873;

(8") C .0190, .0190, .0190, .0190, DSP 6, .019022

$e_x = e_y = 0$, $b^x_g = 2.5$, $b^y_g = 3$, $c^x_g = .5$, $c^y_g = .1$

(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, DSP 3, .075; (8) R/S .062, .062, .062, DSP 4, .0618

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

Prgm. Im

(3)	fLBLA	STO7	hR↓	STO6	hR↓	STO4	hR↓	STO3	hRTN		9
(4)	gLBLfa	fP⇄S	A	fP⇄S	hRTN						14
(5)	gLBLfb	STO9	hR↓	STO8	hR↓	fP⇄S	STO9	hR↓	STO8	fP⇄S	
	hRTN										25
(6)	fLBLB	STOD	fc	fGSB6	+	E	+	CHS	ge^x	hPSE	
	fGSB0	fGSB1	RCL1	STOA	fd	fc	+	fGSB6	+	E	
	+	CHS	ge^x	hPSE	fGSB0	fGSB1	GTOC				52
	fLBL0	↑	↑	2	÷	STO0	+	STO1	hRTN		61
(7,7')	fLBLC	fc	hSTI	fGSB6	STOE	fGSB2	fGSB3	STOA	fGSB1	RCLA	
(8,8")	fd	RCLA	hRTN	GTOC							75
(6')	fLBLD	2	7	3	.	1	5	+	GTOB		84
	fLBL1	RCL1	RCL0	−	STO2	2	÷	−	STO0	hRTN	
	gLBLfd	fc	X	hLSTx	1	●	5	X	fGSB6	+	
	−	RCLA	gx^2	X	1	RCLA	−	fLN	−	fP⇄S	
	STO5	hRTN									116
	fLBL6	RCL6	RCLD	÷	RCL7	−	hRTN				123
	gLBLfc	RCL8	RCLD	÷	RCL9	−	hRTN				130
	fLBL2	RCL1	fe	STOC	RCL0	fe	STOB		hRTN		138
	fLBL3	RCLC	GTO4	fLBL5	RCL1	fe	STOC	fLBL4	RCL0	RCL1	
	−	RCLC	RCLB	−	÷	X	STO+1	RCL1	hF?0	hPSE	
	÷	fRND	fx≠0	GTO5	RCL1	hRTN					164
	gLBLfe	fLN	1	hLSTx	−	gx^2	hLSTx	hRCI	X		
	RCLE	+	X	+	RCL5	+	E	+	hRTN		182
	fLBLE	RCL3	RCLD	÷	RCL4	−	hRTN				189
	fLBL8	STOB	hR↓	fGSB9	RCLB	fGSB9	hRTN				196
	fLBL9	↑	STOA	STO0	EEX	CHS	4	STO2	+	STO1	
	hR↓	fd	hRTN								209
	fLBL7	fc	RCLA	X	fGSB6	+	RCLA	gx^2	X	ge^x	
	RTN										220

R	0	1	2	3	4	5	6	7	8	9
P	x'	x"	Δx	$\Delta H_1^\circ/R$	$\Delta S_1^\circ/R$	d_x	b_h^x	b_s^x	c_h^x	c_s^x
S	y'	y"	Δy	$-\Delta H_2^\circ/R$	$-\Delta S_2^\circ/R$	d_y	b_h^y	b_s^y	c_h^y	c_s^y

A	B	C	D	E	I	Flag 0 is set
x'''	f(y')	f(y")	T	b_y	c_y	
y'''	f(x')	f(x")		b_x	c_x	

Gibbs Energy from Phase Boundaries

When the compositions of saturating phases are known, two constants can be directly determined. If the same b and c values are assumed for both phases for which the same standard states are used,

$$\ln x + b(1-x)^2 + c(1-x)^3 = \ln(1-y) + by^2 + cy^3 = \ln a_1 = \Delta\bar{G}_1/RT$$

$$\ln y + (b+\tfrac{3}{2}c)(1-y)^2 - c(1-y)^3 = \ln(1-x) + (b+\tfrac{3}{2}c)x^2 - cx^3 = \ln a_2 = \Delta\bar{G}_2/RT$$

The mole fraction of component 1 is x in the phase rich in 2 and is 1-y in the phase rich in 1. The simultaneous solution of these equations expressed as $\alpha_1 b + \beta_1 c = \varepsilon_1$ and $\alpha_2 b + \beta_2 c = \varepsilon_2$ is discussed on pg. 114 of reference 13 using the quantities

$$\alpha_1 = 1 - x^2/(1-y)^2, \qquad \alpha_2 = 1 - x^2/(1-y)^2,$$

$$\beta_1 = 1 - x - y^3/(1-x)^2, \qquad \beta_2 = \tfrac{1}{2} + y - \tfrac{3}{2}x^2/(1-y)^2 + x^3/(1-y)^2,$$

$$\varepsilon_1 = [\ln(1-y)/x]/(1-x)^2, \qquad \varepsilon_2 = [\ln(1-x)/y]/(1-y)^2,$$

and $D = \alpha_1\beta_2 - \alpha_2\beta_1$.

When the same b and c values are not expected to be applicable for both phases or if the solubilities are small enough to combine the cubic terms with the square terms, then one uses $\ln\gamma_1/(1-x)^2 = b_x$ and $\ln\gamma_2/(1-y)^2 = b_y$. In addition to calculating values of b and c or b_x and b_y, values of $\ln\gamma_1 = \Delta\bar{G}_1^E/RT$ and $\ln a_1 = \Delta\bar{G}_1/RT$ and the corresponding values for the other components are calculated for both phases. If a set of b and c values or b_x and b_y values have been obtained at several temperatures, steps 4-6 of Prgm. Ωxb can be used to obtain enthalpy and excess entropy terms corresponding to $b = b_h/R + b_s$ or $c = c_h/T + b_s$ and similarily for b_x and b_y. The steps are (4) E, (5) T ↑ b for each b value, then (6) f c will yield b_h and b_s. The same steps are repeated to obtain c_h and c_s values from the set of c values.

Directions:

		Display
(1)	Insert Prgm. yx-bc	
(2)	y ↑ x A	b
(3)	SST	c
(4)	y ↑ x B	b_x
(5)	SST	b_y
(6)	C	$\ln\gamma_1, \ln a_1, \ln\gamma_2, \ln a_2$ for phase rich in 2
(7)	D	$\ln\gamma_2, \ln a_2, \ln\gamma_1, \ln a_1$ for phase rich in 1

NOTE 1: b and c can be obtained after step (5) by RCLE hRCI.

NOTE 2: Steps 6 and 7 can be used in either order following step 3 or step 5.

Prgm. yx-bc Test:

(2) .095 ↑ .07 A 2.4837; (3) SST 0.5397;
(4) .04 ↑ .03 B 3.6889; (5) SST 3.4635;
(6) C 3.4709, -0.0357, 0.0036, -0.0269;
(7) D 3.1920, -0.0269, 0.0051, -0.0357;
after (2), (6) C 2.5823, -0.0769, 0.0160, -0.0566;
(7) D 2.2973, -0.0566, 0.0229, -0.0769.

Prgm. yx-bc

(2)	fLBLA	STO5	1	-	CHS	STO6	hx⇄y	STO3	1	-
	CHS	STO4	RCL5	hx⇄y	÷	STO8	hR↓	RCL3	hx⇄y	÷
	STO7	RCL6	•	5	+	RCL8	gx^2	X	RCL4	+
	CHS	1	•	5	+	STOD	1	RCL7	3	hy^x
	-	RCL6	X	STOC	RCL7	fLN	CHS	RCL4	gx^2	÷
	STO2	1	RCL7	gx^2	-	STOA	RCL8	fLN	CHS	RCL6
	gx^2	÷	STO1	1	RCL8	gx^2	-	STOB	X	hx⇄y
	RCL2	X	-	RCLC	RCLB	X	RCLA	RCLD	X	-
	STO9	÷	hSTOI	RCLC	RCL2	X	RCL1	RCLD	X	-
(3)	RCL9	÷	STOE	hRTN	hx⇄y	hRTN				96
(4)	fLBLB	A	+	hRCI	RCL5	X	-	STOC	RCL3	•
(5)	5	+	hRCI	X	RCLE	+	STOD	RCLC	hRTN	hx⇄y
(6)	fLBLC	hRCI	RCL6	X	RCLE	+	RCL6	gx^2	X	STO0
	RCL5	fLN	+	fa	RCL5	X	-	RCL5	gx^2	X
	↑	STO1	RCL6	fLN	+	RCL0	hR↓	gSTK	hRTN	145
(7)	fLBLD	fa	RCL4	X	-	RCL4	gx^2	X	STO2	RCL3
	fLN	+	hRCI	RCL3	X	RCLE	+	RCL4	gx^2	X
	↑	STO9	RCL4	fLN	+	RCL2	hR↓	gSTK	hRTN	174
	gLBLfa	RCLE	1	•	5	hRCI	X	+	hRCI	hRTN 184

0	1	2	3	4	5	6	7	8	9
	ε_1	ε_2	y	1-y	x	1-x	y/(1-x)	x/(1-y)	D
$\ln\gamma_1^{(2)}$	$\ln\gamma_2^{(2)}$	$\ln\gamma_2^{(1)}$							$\ln\gamma_1^{(1)}$

A	B	C	D	E	I
α_1	α_2	β_1	β_2	b	c
		b_x	b_y		

Calculation of Thermodynamic Properties of Liquid Solution from Properties of Solid Solution and Solidus-Liquidus Data and Effect of Errors

Program Im presents the equations for the solidus-liquidus equilibrium. The same equations and symbols will be used here for Prgm. Ωyxbc. This program starts with enthalpies and entropy of fusion of both components and the partial molal enthalpies and entropies in the solid phase and calculates

$$\Omega_1^\ell = \ln\gamma_1^\ell/x_2^2 \qquad \text{and} \qquad \Omega_2^\ell = \ln\gamma_2^\ell/x_1^2$$

for the liquid phase of composition $x_1^\ell = x$ in equilibrium with the solid phase of composition $x_2^s = y$ and then calculates b_x and c_x of $\Omega_1^\ell = b_x + c_x(1-x)$. It is often of interest to determine the influence of error in x and y on the calculated values of Ω_1 and Ω_2. This program provides values of $d\Omega/dx$ and $d\Omega/dy$ for both components. The variation of each Ω with the change of b_y and c_y can also be calculated. An error in the entropy of fusion of a component causes an error only in Ω^ℓ for the same component. The program gives the error in Ω_2^ℓ for an error in $\Delta S_{f,2}/R$.

$$\ln a_2^s = \ln y + b_y(1-y)^2 + c_y(1-y)^3, \quad \ln a_2^\ell = \ln(1-x) + (b_x + \tfrac{3}{2}c_x - c_x x)x^2$$

$$\ln a_2^\ell - \ln a_2^s = -\Delta G^o_{fus,2}/RT = e_y$$

$$\ln a_2^s + e_y - \ln(1-x) = \ln a_2^\ell - \ln(1-x) = (b_x + \tfrac{3}{2}c_x - e_x x)x^2 = \Omega_2^\ell x^2$$

$$\Omega_2^\ell = [\ln y + b_y(1-y)^2 + c_y(1-y)^3 + e_y - \ln(1-x)]/x^2$$

$$\ln a_1^\ell - \ln a_1^s = -\Delta G^o_{fus,1}/RT = -e_x$$

$$\ln a_1^\ell = \ln x + b_x(1-x)^2 + c_x(1-x)^3$$

$$\ln a_1^s = \ln(1-y) + (b_y + \tfrac{3}{2}c_y)y^2 - c_y y^3$$

$$\ln a_1^s - e_x - \ln x = \ln a_1^\ell - \ln x = (b_x + c_x - c_x x)(1-x)^2 = \Omega_1^\ell(1-x)^2$$

$$\Omega_1^\ell = [\ln(1-y) + (b_y + \tfrac{3}{2}c_y)y^2 - c_y y^3 - e_x - \ln x]/(1-x)^2$$

$$c_x = 2(\Omega_2 - \Omega_1), \quad b_x = 3\Omega_1 - 2\Omega_2 + 2(\Omega_2 - \Omega_1)x = \Omega_1 - c_x(1-x)$$

$$\frac{d\Omega_2^\ell}{d_y} = \left[\frac{1}{y} - 2\,b_y(1-y) - 3c_y(1-y)^2\right]\Big/x^2$$

$$\frac{d\Omega_1^\ell}{d_y} = \left[\frac{1}{1-y} + (2b_y + 2c_y)y - 3c_y y^2\right]\Big/(1-x)^2$$

$$\frac{dc_x}{dv} = 2\left(\frac{d\Omega_2}{dv} - \frac{d\Omega_1}{dv}\right)$$

where $v = x, y, b_y$ or c_y.

cont'd.

$$\frac{d\Omega_2^\ell}{d_x} = \frac{2\ln(1-x)}{x^3} + \frac{1}{x^2(1-x)} - \frac{2\left[x^2\Omega_2^\ell+\ln(1-x)\right]}{x^3} = \frac{1}{x^2(1-x)} - \frac{2\Omega_2^\ell}{x}$$

$$\frac{d\Omega_1^\ell}{dx} = -\frac{1}{x(1-x)^2} - \frac{2\ln x}{(1-x)^3} + \frac{\left[2(1-x)^2\Omega_1^\ell+\ln x\right]}{(1-x)^3} = \frac{-1}{x(1-x)^2} + \frac{2\Omega_1^\ell}{(1-x)}$$

$$\frac{d\Omega_2}{db_y} = \frac{(1-y)^2}{x^2} \qquad \frac{d\Omega_2}{dc_y} = \frac{(1-y)^3}{x^2}$$

$$\frac{d\Omega_1}{db_y} = \frac{y^2}{(1-x)^2} \qquad \frac{d\Omega_1}{dc_y} = \left(\frac{3}{2} - y\right)\frac{y^2}{(1-x)^2}.$$

$$\frac{db_x}{dv} = \frac{d\Omega_1}{dv} - (1-x)\frac{dc_x}{dv} = \frac{d\Omega_1}{dv} - 2(1-x)\left[\frac{d\Omega_2}{dv} - \frac{d\Omega_1}{dv}\right]$$

$$\frac{d\Omega_2^\ell}{d(\Delta S_{f,2}/R)} = \frac{T-T_{MP2}}{Tx^2}, \quad \frac{dc_x}{d(\Delta S_{f,2}/R)} = \frac{2(T-T_{MP2})}{Tx^2}, \quad \frac{db_x}{d(\Delta S_f/R)} = \frac{(2x-2)(T-T_{MP2})}{Tx^2}$$

Directions:	Display
(1) Insert $\Omega yxbc$ tape	
(2) $\Delta H_{f,1}/R \uparrow \Delta S_{f,1}/R$ A	$\Delta H_{f,1}/R$
(3) $-\Delta H_{f,2}/R \uparrow -\Delta S_{f,2}$, $b_h^y \uparrow b_s^y$ R/S	$-\Delta H_{f,2}/R$
(4) $c_h^y \uparrow c_s^y$ R/S	c_h^y
(5) T B	$b_y+\frac{3}{2}c_y$
(6) $y \uparrow x$ C	Ω_2 Ω_1 c_x b_x
(7) D	$d\Omega_2/d_y$ $d\Omega_1/d_y$ $d\Omega_2/d_x$ $d\Omega_1/d_x$
(8) E	$d\Omega_2/db_y$ $d\Omega_2/dc_y$ $d\Omega_1/db_y$ $d\Omega_1/dc_y$
(9) T_{MP2} fa	$d\Omega_2/d(\Delta S_{f,2}/R)$

cont'd.

NOTE 1: After step 6, steps 7, 8 and 9 can be carried out in any order.

NOTE 2: After step 9, 2X gives $dc_x/d(\Delta S_{f,2}/R)$ which yields $db_x/d(\Delta S_{f,2}/R)$ by multiplication by x-1.

NOTE 3: If liquid thermodynamic data are available and it is desired to calculate solid data from x,y values, the same program can be used with reversal of 1 and 2 and x and y with the following directions:

(2) $-\Delta H_2/R \uparrow -\Delta S_2/R$ A
(3) $\Delta H_1/R \uparrow \Delta S_1/R \uparrow b_h^x \uparrow b_s^x$ R/S
(4) $c_h^x \uparrow c_s^x$ R/S
(5) TB $\rightarrow b_x+\frac{3}{2}c_x$
(6) x ↑ y C $\rightarrow \Omega_1^s, \Omega_2^s, c_y, b_y$

Prgm. Ωyxbc

(2)	fLBLA	fP⇄S	STO4	hR↓	STO3	hP⇄S	hRTN				7
(3)	STO7	hR↓	STO6	hR↓	STO4	hR↓	STO3	hRTN			15
(4)	STO9	hR↓	STO8	hRTN							19
(5)	fLBLB	STOD	h 1/x	RCL6	X	RCL7	-	STO0	RCL8	RCLD	
	÷	RCL9	-	STO5	fP⇄S	CHS	STO5	3	X	2	
	÷	-	STO0	fP⇄S	hRTN						44
(6)	fLBLC	fP⇄S	STO1	1	-	CHS	STO2	fP⇄S	hR↓	STOA	
	1	hx⇄y	-	STOB	hLSTx	fe	+	fP⇄S	RCL2	fLN	
	-	RCL1	gx^2	÷	STO9	f-x-	RCLB	fe	-	RCL1	
	fLN	-	RCL2	gx^2	÷	STO8	f-x-	RCL9	-	2	
	X	CHS	STO7	f-x-	RCL2	X	RCL8	-	CHS	STO6	
	fP⇄S	hRTN									96
	gLBLe	fLN	1	hLSTx	-	gx^2	hLSTx	RCL5	X	RCL0	
	+	X	+	RCL3	RCLD	÷	RCL4	-	hRTN		115
(7)	fLBLD	RCLB	RCLB	RCL5	X	3	X	RCL0	2	X	
	+	X	RCLA	h 1/x	-	CHS	fP⇄S	RCL1	gx^2	÷	
	hLSTx	f-x-	RCLA	RCLA	RCL5	X	3	X	RCL0	2	
	X	+	X	RCLB	h 1/x	-	RCL2	gx^2	÷	STOE	
	f-x-	RCL9	2	X	RCL1	RCL2	X	h 1/x	-	RCL1	
	÷	CHS	STOC	f-x-	RCL8	2	X	RCL1	RCL2	X	
	h 1/x	-	RCL2	÷	fP⇄S	STO1	RCLC	STO2	hR↓	hRTN	185
(8)	fLBLE	fP⇄S	RCLB	RCL1	÷	gx^2	STOC	f-x-	RCLB	X	
	f-x-	RCLA	RCL2	÷	gx^2	f-x-	1	.	5	RCLA	
	-	X	fP⇄S	hRTN							209
(9)	gLBLa	RCLD	-	hLSTx	÷	fP⇄S	RCL1	gx^2	÷	CHS	
	fP⇄S	hRTN									221

RP	0	1	2	3	4	5	6	7	8	9
	b_y	$\frac{d\Omega_1}{d_x}$	$\frac{d\Omega_2}{d_x}$	$-\Delta H_2/R$	$-\Delta S_1/R$	c_y	b_h^y	b_s^y	c_h^y	c_s^y

RS	0	1	2	3	4	5	6	7	8	9
	$b_y+\frac{3}{2}c_y$	x	1-x	$\Delta H_1/R$	$\Delta S_1/R$	$-c_y$	b_x	c_x	Ω_1	Ω_2

A	B	C	D	E	I
y	1-y	$d\Omega/d_x, d\Omega_2/db_y$	T	$\frac{d\Omega_1}{dy}$	$\frac{d\Omega_2}{dy}$

TEST: (2) 4300 ↑ 1.487 A; (3) -2184 ↑ -0.993 ↑ 2500 ↑ 0 R/S; (4) 200 ↑ 0 R/S; (5) 2773 B 1.010; (6) .10 ↑ .78 C 0.328, 1.848, -3.040, 2.517; (7) D 13.481, -18.829, 6.629, -9.686; (8) E 1.331, 1.198, 0.207, 0.289; (9) 2199 fa 0.340; 2X, 0.680; (0.781-1)X, 0.150.

If it is desired to determine the effect upon b_x and c_x of the liquid phase of errors in b_y and c_y of the solid phase, Prgm. bc calculates dc_x/db_y, dc_x/dc_y, db_x/db_y, and db_x/db_y.

$$\frac{dc_x}{db_y} = 2\left(\frac{d\Omega_2}{db_y} - \frac{d\Omega_1}{db_y}\right) = 2\left[\frac{(1-y)^2}{x^2} - \frac{y^2}{(1-x)^2}\right]$$

$$\frac{dc_x}{dc_y} = 2\left(\frac{d\Omega_2}{dc_y} - \frac{d\Omega_1}{dc_y}\right) = 2\left[\frac{(1-y)^3}{x^2} - (\tfrac{3}{2}-y)\,\frac{y^2}{(1-x)^2}\right]$$

$$\frac{db_x}{db_y} = \frac{d\Omega_1}{db_y} - (1-x)\,\frac{dc_x}{db_y} = \frac{d\Omega_1}{db_y} - 2(1-x)\left[\frac{d\Omega_2}{db_y} - \frac{d\Omega_1}{db_y}\right]$$

$$= \frac{y^2}{(1-x)^2} - 2(1-x)\left[\frac{(1-y)^2}{x^2} - \frac{y^2}{(1-x)^2}\right]$$

$$\frac{db_x}{dc_y} = \frac{d\Omega_1}{dc_y} - (1-x)\frac{dc_x}{dc_y} = \frac{d\Omega_1}{dc_y} - 2(1-x)\left[\frac{d\Omega_2}{dc_y} - \frac{d\Omega_1}{dc_y}\right]$$

$$= (\tfrac{3}{2}-y)\,\frac{y^2}{(1-x)^2} - 2(1-x)\left[\frac{(1-y)^3}{x^2} - (\tfrac{3}{2}-y)\,\frac{y^2}{(1-x)^2}\right]$$

Directions:

	Display
(1) Insert tape bc	
(2) y ↑ x A	dc_x/db_y dc_x/dc_y db_x/db_y db_x/db_y

Prgm. bc

fLBLA	STOA	1	-	CHS	STOB	hR↓	STOC	1	-	
CHS	STOD	RCLA	÷	gx^2	STO9	RCLC	RCLB	÷	gx^2	
STO8	-	2	X	STO2	f-x-	RCL9	RCLD	X	RCL8	
1	•	5	RCLC	-	X	STO7	-	2	X	
STO3	f-x-	RCL8	1	RCLA	-	RCL2	X	-	STO0	
f-x-	RCL7	1	RCLA	-	RCL3	X	-	STO1	hRTN	60

---

cont'd.

0	1	2	3	7	8	9
$\frac{db_x}{db_y}$	$\frac{db_x}{dc_y}$	$\frac{dc_y}{db_y}$	$\frac{dc_x}{dc_y}\left(\frac{3}{2}-y\right)$	$\left(\frac{y}{1-x}\right)^2$	$\left(\frac{y}{1-x}\right)^2$	$\left(\frac{1-y}{x}\right)^2$
		A	B	C	D	
		x	1-x	y	1-y	

TEST: 0.38 ↑ 0.42 A 3.50, 1.74, -1.60, -0.53

There is no general procedure for applying the various programs that have been described for treating a phase diagram. Liquidus data usually would be treated first by Prgm. Ωxb which neglects the effect of solid solubility to obtain a rough idea of the partial molal enthalpies and entropies in the liquid phase. Neglect of solid solubility or experimental error in the data can yield values substantially in error and the initial values may have to be somewhat modified to be within the range of reasonable values indicated by various theoretical models. Program Im can be used to calculate the boundaries of the solidus and liquidus from the selected thermodynamic values. There are, in general, an infinite combination of thermodynamic quantities that will fit a set of experimental data within experimental error. Comparison of the results from Prgm. Im with the original experimental data will indicate what changes in the thermodynamic data might be necessary to give a better fit and still be in the range of reasonable entropy and enthalpy values. Program yx-bc is of use of obtain Gibbs energy values from boundary values at a given temperature or Prgm. Ωyxbc will yield the molefraction dependence of the thermodynamic properties in one phase knowing the properties in the saturating phase. This last program can be of value in adjusting the thermodynamic data through analysis of the effect of error in various quantities upon the phase boundaries and the effect of error in one thermodynamic quantity upon related thermodynamic values. For intermediate phases with relatively limited solid solubility, the next program, Prgm. SP, is often of value. Because of the experimental error in most observations and the resulting wide spread of thermodynamic quantities that could be used to fit the data, it is important that this fitting process not be carried out in a mechanical manner. Considerable judgment using theoretical models with useful predictive value is essential to narrow down the range of thermodynamic values consistent with the experimental data.

Solubility Product Calculations for Liquidus of Intermediate Phases

Combination of the equations $\Delta G^\circ/RT = (\Delta G^\circ - \Delta H^\circ_{298})/RT + \Delta H^\circ_{298}/RT$ for $A(s) + nB(s) = AB_n(s)$, $A(s) = A(\ell)$, and $nB(s) = nB(\ell)$ gives for $AB_n(s) = A(\ell) + nB(\ell)$, $-\Delta G^\circ/RT = -\Delta H^\circ_{298}/RT - (\Delta G^\circ - \Delta H^\circ_{298})/RT = \ln K = \ln x_A + n\ln x_B + \ln\gamma_A + n\ln\gamma_B = \ln x_A + n\ln x_B - (b_s - b_h/T)(1-x_A)^2 - (c_s - c_h/T)(1-x_A)^3 - n[b_s + \frac{3}{2}c_s - (b_h + \frac{3}{2}c_h)/T]x_A^2 + n(c_s - c_h/T)x_A^3$.

$$T = \frac{\Delta H_{298}/R + [b_h + c_h(1-x_A)](1-x_A)^2 + n[b_h + \frac{3}{2}c_h - c_h x_A]x_A^2}{-\left(\frac{\Delta G - \Delta H^\circ_{298}}{RT}\right) - \ln x_A - n\ln(1-x_A) + [b_s + c_s(1-x_A)](1-x_A)^2 + n(b_s + \frac{3}{2}c_s - c_s x_A)x_A^2}$$

$$-\Delta G^\circ/RT = \ln x_A + n\ln(1-x_A) + \frac{[b_h + c_h(1-x_A)](1-x_A)^2 + n[b_h + \frac{3}{2}c_h - c_h x_A]x_A^2}{T} - [b_s + c_s(1-x_A)](1-x_A)^2 - n[b_s + \frac{3}{2}c_s - c_s x_A]x_A^2$$

Program SP can be used to calculate the liquidus curve when $\Delta H^\circ_{298}/R$ is known or to calculate $\Delta H^\circ_{298}/R$ when the liquidus curve is known.

Directions:

(1) Insert Prgm. SP

(2) b_h ↑ c_h ↑ b_s ↑ c_s E

(3) $\Delta H^\circ_{298}/R$ STOA, $-(\Delta G - \Delta H^\circ_{298})/RT$ STOB n STOE, 273.15 STO3

(4) x_A A → T

(5) R/S → t

(6) x_A ↑ T B → $-\Delta G^\circ/RT$

(7) R/S → $\Delta H^\circ/R$

A	B	C	D	E
$\Delta H^\circ_{298}/R$	$-(\Delta G^\circ - \Delta H^\circ_{298})/RT$	x_A	$1-x_A$	n
RP	0	1	2	3
	b_h	c_h	used	273.15
RS	b_s	c_s		

cont'd.

Prgm. SP

fLBLE	fP⇄S	STO1	hR↓	STO0	hR↓	fP⇄S	STO1	hR↓	STO0	
hRTN										11
fLBLA	STOC	1	−	CHS	STOD	fGSBO	RCLA	+	STO2	
fP⇄S	fGSBO	fP⇄S	RCLB	+	RCLD	fLN	RCLE	X	−	
RCLC	fLN	−	RCL2	hx⇄y	÷	hRTN	RCL3	−	hRTN	
RCL3	−	hRTN								44
fLBL0	1	•	5	RCLC	−	RCL1	X	RCL0	+	
RCLE	X	RCLC	gx^2	X	RCLD	RCL1	X	RCL0	+	
RCLD	gx^2	X	+	hRTN						69
fLBLB	STO4	hR↓	STOC	1	−	CHS	STOD	fLN	RCLE	
X	RCLC	fLN	+	fGSBO	RCL4	÷	+	fP⇄S	fGSBO	
fP⇄S	−	hRTN	RCLB	−	RCL4	X	CHS	hRTN		98

Chapter IV

Regular Solution Calculations

The previous chapters have frequently referred to regular solution equations and their application to thermodynamic calculations.(12,19,20) In Chapter III, it was pointed out that the partial molal Gibbs energies expressed in terms of volume fractions as composition variables can be conveniently expanded in terms of mole fraction truncated at the cubic term. In its simplest form, the regular solution theory is a pair-interaction model with interactions between unlike atoms or molecules being taken as the geometric mean of the interactions between like atoms of molecules and excess entropy contributions comes only from the temperature coefficients of the volume and energy of sublimation terms. For most actual systems, the geometric mean assumption must be modified and additional entropy contributions must be considered. For metallic atoms, there is also the question of the appropriate valence state to use for evaluating the cohesive energy(7).

The programs tabulated below can use for ΔH either the enthalpy of sublimation to the ground electronic state or to any valence state in obtaining the first approximations to the solubility parameters. Subsequent approximations depend upon the types of atoms being mixed and an appraisal of the types of chemical interactions that can take place. Thus strain contributions due to size disparity can add positive contributions to the Gibbs energy of mixing for solids with equivalent lattice positions and can add negative contributions for appropriate size differences for structures such as those of the Laves phases, liquids, and other systems with non-equivalent sites that achieve better space filling with appropriate size disparities. The very substantial acid-base interactions that can take place when atoms with non-bonding electrons are mixed with atoms with unoccupied low energy orbitals must also be considered.(8) However, the simplest form of internal pressure calculation is the starting point for most systems. For this level of approximation, the energy of vaporization is taken as $\Delta H - RT_i$ where T_i is the average temperature of the range of interest.

$$T\Omega_1 = T\ln\gamma_1/(1-x_1)^2 = V_1(\delta_n-\delta_1)^2/R = V_1\left\{\left[\left(\frac{\Delta H_n}{R} - T_i\right)/V_n\right]^{\frac{1}{2}} - \left[\left(\frac{\Delta H_1}{R} - T_i\right)/V_1\right]^{\frac{1}{2}}\right\}^2$$

$$T\Omega_n = T\ln\gamma_n/x_1^2 = V_n(\delta_n-\delta_1)^2/R$$

$$T_{critical} = [2V_n(\delta_n-\delta_1)^2/R]/[1+(V_n/V_1)^{\frac{1}{2}}]^2$$

Program RS can store data for eight binary systems of component 1.

Directions:	Display
(1) Insert Prgm. RS	
(2) R ↑ T_i ↑ ΔH_1 ↑ V_1 A	$[(\Delta H_1/R-T_i)/V_1]^{\frac{1}{2}}$
(3) B	2
(4) ΔH_n ↑ V_n C; repeat for all n up to n = 9	$V_1(\delta_n-\delta_1)^2/R$, $V_n(\delta_n-\delta_1)^2/R$
(5) T ↑ n D	$\Omega_1=\ln\gamma_1/x_n^2$, $\Omega_n=\ln\gamma_n/x_1^2$
(6) n E	$T_{critical}$ for 1-n system

NOTE 1: Step 3 is required before a new set of data in step 4.

NOTE 2: Steps 5 and 6 can be used in any order. If it is desired to add more values in step 4 after step 5 or 6 has been used, carry out step 6 for last value of n used in step 4. Then key f b and step 4 will accept values for n+1, n+2, etc. up to the maximum of 9.

Prgm. RS

(2)	fLBLA	STOA	hR↓	STOB	hR↓	STOC	hR↓	STOE	RCLB	hx⇄y	
	÷	RCLC	−	RCLA	÷	f√x	STOD	hRTN			18
(3)	fLBLB	2	hSTI	hRTN							22
(4)	fLBLC	STO0	hR↓	STO1	RCLE	÷	RCLC	−	RCL0	÷	
	f√x	RCLD	−	gx^2	↑	STO(i)	fa	RCL0	STO(i)	X	
	fb	hx⇄y	RCLA	X	f-x-	hR↓	hRTN				49
(5)	fLBLD	hSTI	hR↓	RCL(i)	hx⇄y	÷	↑	↑	fa	RCL(i)	
	X	hx⇄y	RCLA	X	f-x-	hR↓	hRTN				66
(6)	fLBLE	hSTI	RCL(i)	2	X	fa	RCL(i)	X	RCL(i)	RCLA	
	÷	f√x	1	+	gx^2	÷	hRTN				83
	gLBLfa	hRCI	1	0	+	hSTI	hR↓	hRTN			91
	gLBLfb	hRCI	9	−	hSTI	hR↓	hRTN				98

	A	B	C	D	E	I
	V_1	ΔH_1	T_i	$\left(\frac{\Delta H_1/R-T_i}{V_i}\right)^{\frac{1}{2}}$	R	Index

P	0	1	2	3	.....	8	9
	V_n	ΔH_n	$(\delta_1-\delta_2)^2/R$	$(\delta_1-\delta_3)^2/R$	.....	$(\delta_1-\delta_8)^2/R$	$(\delta_1-\delta_9)^2/R$
S		2	3	.....		8	9
		V_2	V_3	.....		V_8	V_9

Use of Regular Solution Equations for Fitting of Data

When there is substantial solid and liquid solubility and Prgm. Im of Chapter III is required, an exact analytical solution cannot be given, but quite accurate fitting of the results can be obtained in terms of a polynomial fit of the deviation from simple limiting equations.

If the solid and liquid solubilities are small, the liquidus of component A of an A-B binary system is given by $\ln x_A^L = \alpha + a_{-1}T^{-1}$ where

$$\alpha = \Delta S_f^o/R + b_s^L + c_s^L \qquad \text{and} \qquad a_{-1} = -\Delta H_f^o/R - b_h^L - c_h^L$$

and all quantities refer to component A. The solidus can be expressed as

$$\ln x_B^s = \alpha^s + a_{-1}^s T^{-1}$$

where

$$\alpha^s = -\Delta S_f^o/R + b_s^S + c_s^S \qquad \text{and} \qquad a_{-1}^S = \Delta H_f^o/R - b_h^S - c_h^S$$

and all quantities refer to component B.

Actual data are fitted to the equation $\ln x = a_{-1}T^{-1} + \Delta$, where Δ is a power series in T. It is sometimes useful to fit $\ln \frac{x}{T_f-T} = a_{-1}T^{-1}+\Delta$. When the liquidus or solidus is of very limited extent near the melting point, a simpler equation can be used. The limiting liquidus near the melting point of B becomes

$$\frac{x_A^L}{(T_f-T)} = \frac{\Delta S_f^o/R}{T(1-x_A^S/x_A^L)}$$

from Eq.(19-14) of ref.(12) which reduces to

$$\frac{x_A^L}{(T_f-T)} = \frac{\Delta S_f^o/R}{T}$$

when solid solubility is small.

The various modifications of these limiting equations can be used to obtain accurate least square fits for liquidus or solidus boundaries to a polynomial with a minimum number of terms. Prg. LSΔ is designed to handle the variety of situations that might arise by evaluating the constants of $f(x,T) = a_{-1}/T + a_0 + a_1T + a_2T^2$, where $f(x,T)$ may be $\ln[x/(T_f-T)]$, $\ln x$, or $x/(T_f-T)$. a_{-1} is fixed as indicated below by the type of equilibrium and $\Delta = f(x,T) - a_{-1}/T$ is fit to a power series in T or under some circumstances in T_f-T.

Prgm. LSΔ for $f(x,T) = \frac{a_{-1}}{T} + \Delta$, $\Delta = a_0 + a_1T + a_2T^2$

		Display
(1)	Insert tape LSΔ	
(2)	Store a_{-1} in B	a_{-1}
(3)	fa to clear registers	a_{-1}
(4)	Modify prgm. to fit $f(x,T) = x/(T_f-T)$ or lnx in place of $\ln \frac{x}{2890-T}$	
(5)	x_1 T_1 B	$T_1^2\Delta$
	If any of T values are evenly spaced, key xA after 2nd of regularly spaced values if 10^{-2} has been replaced by proper I.	
(6)	R/S	a_0
(7)	SST SST	a_1 , a_2
(8)	T D	x
	E after 2nd of regularly spaced T	x
(9)	C, SST	a_1', a_0' for T_f-T in place of T
(10)	T fd	x
	fe for evenly spaced T	x

NOTE 1: Prgm. is set for $f(x,T) = \ln \frac{x}{2890-T}$, although usually a simpler function is used.

NOTE 2: For $f(x,T) = \ln x$, remove fGSB 1- in 3rd line (steps 22-3) and fGSB1 + near end of LBL D (steps 132-3 minus 2) and if T_f-T power series be used, remove hR↑ fLN + of gLBLd, step 192.

NOTE 3: If x is keyed in as $10^n x$, add EEX n ÷ in 3rd line (after hR↑ of step 20)

NOTE 4: For melting point of metal other than Mo, replace 2890 by T_f after fLBL1, fLBLC, and end of gLBLd.

NOTE 5: For even spaced temp. at intervals I other than 100°, replace EEX 2 by I after fLBLA, fLBLE, and gLBLd.

NOTE 6: If x is to be used instead of lnx, remove fLN in 3rd line (step 21), and remove ge^x at end of fLBLE and end of gLBLe.

NOTE 7: For an A-B system with $\ln \gamma_A = bx_B^2 + cx_B^3$ and $\ln \ _B = (b+\frac{3}{2}c)x_A^2 - cx_A^3$, there are the following combinations of f(x,T) and a_{-1}.

Solid-Liquid Equilibrium	$f(x,T)$	a_{-1}
A liquidus, low x_A^L	$\ln x_A$	$-\Delta H_{f,A}-b^L-c^L$
A solidus, low x_A^L	$\ln x_B$	$\Delta H_{f,B}-b^S-c^S$
A liquidus, high x_A^L	$x_B/(T_{f,A}-T)$	$\Delta S_{f,A}$
A solidus, high x_A^L	$\ln x_B$ or $\ln[x_B/(T_{f,A}-T)]$	$\Delta H_{f,B}-(b^S-b^L)-\frac{1}{2}(c^S-c^L)$
B liquidus, high x_B^L	$x_A/(T_{f,B}-T)$	$\Delta S_{f,B}$
B solidus, high x_B^L	$\ln x_A$ or $\ln[x_A/(T_{f,B}-T)]$	$\Delta H_{f,A}-(b^S-b^L)-(c^S-c^L)$
Solid-Solid Equilibrium		
A solidus	$\ln x_B$	$-b^S-\frac{1}{2}c^S$
B solidus	$\ln x_A$	$-b^S-c^S$

Prgm. LSΔ

```
gLBLA   RCLB    fCLREG  fP⇄S    fCLREG  STOB    hRTN                            7
fLBLA   RCLE    EEX     2       +       fLBLB   STOE    ↑       ↑       gx²
Σ+      hLSTx   hR↑     fLN     fGSB1   -       RCLB    RCLE    ÷       -
fP⇄S    Σ+      hLSTx   RCLE    X       STO+1   fP⇄S    hRTN                    35
RCL4    RCL8    fP⇄S    STO2    hR↓     STO0    RCL9    ÷       STO4    RCL6
gx²     RCL9    ÷       RCL7    -       hLSTx   RCL6    RCL9    ÷       X
RCL8    -       STO3    hx⇄y    STO8    RCL7    gx²     RCL9    ÷       RCL5
-       STO5    RCL1    RCL2    RCL4    RCL7    X       hx⇄y    -       hSTI
RCL4    RCL6    X       hR↑     -       STOE    RCL8    RCL5    X       RCL3
gx²     -       RCLE    RCL5    X       RCL3    hRCI    X       -       hx⇄y
÷       STOC    RCL8    X       RCLE    hx⇄y    -       RCL3    ÷       STOD
RCL7    X       RCL6    RCLC    X       +       RCL9    ÷       RCL4    hx⇄y
-       STOA    hRTN    RCLC    RCLD                                            120
fLBLE   hR↑     EEX     2       +       fLBLD   fb      RCLB    hR↑     ÷
+       fGSB1   +       ge^x    hRTN                                            135
fLBL1   2       8       9       0       hR↑     -       fLN     hRTN            144
gLBLb   ↑       ↑       ↑       RCLD    X       RCLC    +       X       RCLA
+       hRTN                                                                    156
fLBLC   2       8       9       0       fb      STO3    hR↑     RCLD    X
2       X       RCLC    +       CHS     STO4    hRTN    RCL3                    174
gLBLd   hR↑     EEX     2       +       gLBLe   ↑       ↑       ↑       RCLD
X       RCL4    +       X       RCL3    +       hR↑     fLN     +       2
8       9       0       hR↑     -       RCLB    hx⇄y    ÷       +       ge^x
hRTN                                                                            205
```

	0	1	2	3	4	5	6	7	8	9
RS		$\Sigma T\Delta$			ΣT^2	ΣT^4	ΣT	ΣT^2	ΣT^3	i
then										
RP	$\Sigma\Delta$		$\Sigma T^2\Delta$	s	$\frac{1}{i}\Sigma\Delta$	r			q	
				a_1'	a_2'					
					4	5	6	7	8	9
RP					$\Sigma\Delta$	$\Sigma\Delta^2$	ΣT^2	ΣT^4	$\Sigma T^2\Delta$	i
then										
RS										

	A	B	C	D	E	I
		a_{-1}			T	
	a_0		a_1	a_2	t	u

A fifth chapter entitled "Philosophy of Critical Evaluation and Compilation" has been written which describes the compilation procedures and use of some of the programs described in the earlier chapters and which particularily reviews some of the bonding models used to predict thermodynamic values for systems lacking data. Because of the length of the present report, the decision was made to issue the fifth chapter as a separate report (LBL-7666) and the present summary of calculation programs will be ended with a program used to estimate enthalpies of formation using the Rittner model for gaseous halides with a large ionic component.

Bonding Energies of Gaseous Halides Using the Rittner Model

Rittner (24) has used an ionic model including polarizability to calculate bonding energies of gaseous halides. There are a number of difficulties in the model having to do with the proper treatment of overlap repulsion, the appropriate value of the polarizability to be used, and the contribution of higher order terms. In spite of the limitations, Cubicciotti (25,27) and Hildenbrand (26) have reported success in using the model for compounds of highly charged cations and criteria have been developed to predict range of applicability of the model.

It is of interest to determine how far the model can be extended among the gaseous transition metal halides, for which thermodynamic data are very scanty. It would be useful to compare the calculated values with the available experimental data to determine if the model or some modification of the model might yield useful data. The HP-67 calculator program given below follows the calculations of Cubicciotti, Hildenbrand, et al.(27). Enthalpies of formation or dissociation energies to the gaseous ions can be readily calculated for MX, linear MX_2, planar MX_3, and tetrahedral MX_4 given a value of the cation-anion distance and the polarizabilities. These molecules will be described as MX_n with x=1 to 4. The operation of the program will be illustrated using typical parameters for Zr and Mo.

$$H_0^\circ/R = 167\,103[a_n/r + \alpha b_n/r^4] \quad \text{for}$$

(1) $$M^{n+}(g) + nX^-(g) = MX_n(g)$$

where α is the anion polarizability in A^3 for the symmetrical molecules and is the sum of the anion and cation polarizabilities for MX molecules. The constant 167 103, given by $e^2N_0/10^{-8}R = e^2/10^{-8}k = (4.80324)^2 10^4/1.38065$, yields values of $\Delta H_0^\circ/R$ in Kelvin units when r is given in Å. The values of a_n and b_n are (27):

$$a_1 = -\tfrac{10}{11} \qquad b_1 = -\tfrac{7}{11}$$
$$a_2 = -\tfrac{10}{11}(3.5) \qquad b_2 = -\tfrac{7}{11}(\tfrac{49}{16})$$
$$a_3 = -\tfrac{10}{11}(9-\sqrt{3}) \qquad b_3 = -\tfrac{7}{11}(8.17)$$
$$a_4 = -\tfrac{10}{11}(15-3\sqrt{1.5}) \qquad b_4 = -\tfrac{7}{11}(16.48)$$

where $\frac{10}{11} = 1 - \frac{1}{p}$ and $\frac{7}{11} = 1 - \frac{4}{p}$ with p, the power of the overlap repulsion term, taken equal to 11.

The value of $\Delta H_0^\circ/R$ for $M(s) + \frac{n}{2}X_2 = M^{n+}(g) + nX^-(g)$ is given by the sum of ΔH_0° for the following reactions.

(2) $M(s) = M(g)$

(3) $\frac{n}{2} X_2 = \frac{n}{2} X(g)$

where X_2 is taken as gaseous for F_2 and Cl_2 at 0K and solid for Br_2 and I_2.

(4) $nX(g) + ne^-(g) = nX^-(g)$

(5) $M(g) = M^{n+}(g) + ne^-(g)$.

For reaction (2), $\Delta H_0^\circ/R$ = 78970±250K was used (29) for Mo and 72560±500K was used (28) for Zr. For reaction (3), $\Delta H_0^\circ/R$ was taken (30-35) as 9 240±70 for F, 14 386±1 for Cl, 14 185±5 for Br, and 12 889±2 K for I. For reaction (4), $\Delta H_0^\circ/R$ was taken (36,37) as -39 440±20 for F, -41 930±30 for Cl, -39 030±30 for Br, and -35 550±30K for I. The ionization potentials in cm^{-1} from Moore (38) for

Mo^+ 57 260, Mo^{2+} 130 300, Mo^{3+} 219 100, Mo^{4+} 374 180
Zr^+ 55 145, Zr^{2+} 105 900, Zr^{3+} 185 400 and Zr^{4+} 276 970

are used to calculate $\Delta H_0^\circ/R$ for reaction(5). The sum of $\Delta H_0^\circ/R$ values for reactions (1) to (5) yields $\Delta H_0^\circ/R$ for the formation from the elements.

(6) $M(s) + \frac{n}{2} X_2(g) = MX_n(g)$

$$\Delta H_{298}^\circ/R = \Delta H_0^\circ/R + (H_{298}^\circ-H_0^\circ)/R_{MX_n} - (H_{298}^\circ-H_0^\circ)/R_M - \frac{n}{2}(H_{298}^\circ-H_0^\circ)/R_{X_2}.$$

For M(s), $(H_{298}^\circ-H_0^\circ)/R$ = 552K for Mo and 665K for Zr. For gaseous X_2, $\frac{1}{2}(H_{298}^\circ-H_0^\circ)/R$ = 531 for F_2 and 552 for Cl_2. For $Br_2(\ell)$ at 298K, $\frac{1}{2}(H_{298}^\circ-H_0^\circ)/R$ = 1474K and for $I_2(s)$, $\frac{1}{2}(H_{298}^\circ-H_0^\circ)/R$ = 794K. Values of $(H_{298}^\circ-H_0^\circ)/R$ for $MX_n(g)$ are tabulated in Table A.

The calculation of $\Delta H_{298}^\circ/R$ for reaction(6) can be expressed as $\Delta H_{298}^\circ/R = U/R + M_n + nX_x + (H_{298}^\circ-H_0^\circ)/R_{MX_n}$, where $\Delta H_0^\circ/R$ for reaction(1) is expressed as $U/R = A_n/r + \alpha B_n/r^4$ with A_n = 167 103 a_n and B_n = 167 103 b_n, M_n is the sum of the $\Delta H_0^\circ/R$ values of reactions(2) and (5) minus $(H_{298}^\circ-H_0^\circ)/R$ for M(s), and X_x is the sum of $\Delta H_0^\circ/R$ values of reactions(3) and (4) minus $(H_{298}^\circ-H_0^\circ)/R$ for $\frac{1}{2}X_2$. The M_n values are calculated by step 5 of the program. The other values, along with α_x values, are tabulated as follows:

n	A_n	B_n		X_x	$\alpha, Å^3$
1	-151 912	- 53 169	F	-30 730	1.2
2	-531 691	-325 660	Cl	-28 100	3.0
3	-1 104 087	-868 800	Br	-26 320	4.5
4	-1 872 429	-1 752 500	I	-23 450	6.42

The α value for I is from Cubicciotti, Hildenbrand, et al.(27). The other values are from Dalgarno (39). The calculation is carried out in two stages. After storing A_n and B_n, U/R is calculated from the M-X distance r by $U/R = A_n/r + \alpha B_n/r^4$. Then the value of U/R is combined with $(H^\circ_{298}-H^\circ_0)/R$ of MX_n, to calculate $\Delta H^\circ_{298}/R$ of reaction(6). Constants are stored in registers or are inserted with a data card as indicated.

RP	0	1	2	3	4	5	6	7	8	9
	r	A_1	A_2	A_3	A_4	1.4388	X_F	X_{Cl}	X_{Br}	X_I

RS	1	2	3	4	6	7	8	9
	B_1	B_2	B_3	B_4	M_1	M_2	M_3	M_4
	A	B	C	D	E	I		
	X_x	M_n	A_n	$\alpha_x B_n$	R	6-9		
						n		
						n+10		
						n+15		

TABLE A Values of $(H^\circ_{298}-H^\circ_0)/R$ in K

n	MoF_n	$MoCl_n$	$MoBr_n$	MoI_n	ZrF_n	$ZrCl_n$	$ZrBr_4$	ZrI_4
1	1079	1141	1176	1221	1092	1132	1172	1213
2	1624	1948	2080	2200	1423	1783	1872	1842
3	1768	2104	2395	2570	1817	2119	2321	2930
4	2274	2678	2987	3168	2278	2713	3001	3185

Directions:

(1)	Insert Prgm. I	
(2)	Insert Data Tape I	Display
(3)	$\alpha \uparrow n \uparrow r \uparrow$ 6 for F, 7 for Cl 8 for Br, or 9 for I A	U/R of $MX_n(g)$
(3a)	If calculation is to be repeated for different n with same X, $\alpha \uparrow n \uparrow r$ B	U/R of $MX_n(g)$
(4)	With U/R displayed, key $(H_{298}-H_0)/R$ of MX_n R/S	$\Delta H^\circ_{298}/R$ of $MX_n(g)$
(5)	To insert data for different M, $\Delta H^\circ_0/R$ subl. of M $\uparrow (H^\circ_{298}-H^\circ_0)/R$ of M(s) E $IP_4 \uparrow IP_3 \uparrow IP_2 \uparrow IP_1 \uparrow$ R/S	1.44 M_4
(6)	fa to multiply any value by R	
(7)	fe to divide any value by R	

NOTE 1: α is α_x of halide ion except for n = 1 where sum of α values of anion and cation are used.

NOTE 2: Step 2 leaves registers prepared for fluoride calculations. One can go directly from step 2 to step 3a for MF_n calculations.

Prgm. I

(3)	fLBLA	hSTI	hR↓	RCLi	STOA	hR↓	fLBLB	STO0	hR↓	hSTI	
	hR↓	RCLi	STOC	hR↓	hRCI	1	0	+	hSTI	hR↓	
	RCLi	X	STOD	hRCI	5	+	hSTI	RCLi	STOB	RCL0	
	$h\frac{1}{x}$	RCLC	hx⇄y	X	RCLD	hLSTx	4	hy^x	X	+	
	hRTN										44
(4)	+	hRCI	1	5	−	RCLA	X	+	RCLB	+	
	hRTN										52
(5)	fLBLE	1	9	hSTI	hR↓	−	STOi	fDSZ	STOi	fDSZ	
	STOi	fDSZ	STOi	RCL5	STO0	hRTN					68
	STOX0	hR↓	RCL0	STO+i	fISZ	hR↓	RCL5	X	RCL0	+	
	fGSB0	fGSB0	STO+i	RCLi	STOB	hRTN					84
	fLBL0	STO+i	fISZ	hx⇄y	RCL5	X	+	hRTN			92
(6)	gLBLa	RCLE	X	hRTN							96
(7)	gLBLe	RCLE	÷	hRTN							100

TEST:

(2) RP 0 1 2 3 4 5

hREG, 0 -151 912 -531 691 -1 104 087 -1 872 429 1.4388

6	7	8	9	A	B	C	D	E	I
-30 730	-28 100	-26 320	-23 450	-30 730	0	0	0	1.98719	0

RS	1	2	3	4	6	7	8	9
	- 53 169	-32560	-868800	-1752500	160802	348275	663510	1201871

(3a) 1.2 ↑ 4 ↑ 1.82 B -1220477, (4) 2274 R/S -139252
(3a) 8.2 ↑ 1 ↑ 1.82 B -123204, (4) 1079 R/S 7947
(3) 3 ↑ 4 ↑ 2.26 ↑ 7 A -1030041, (4) 2678 R/S 62108
(3a) 10 ↑ 1 ↑ 2.26 B -87599, (4) 1141 R/S 46245
(3) 6.42 ↑ 3 ↑ 2.66 ↑ 9 A -526481, (4) 2570 R/S 69249
(5) 78970 ↑ 552 E 1.44, 374180 ↑ 219100 ↑ 130300 ↑ 57260 R/S 1201871,
(6) fa 2388347 (7) fe 1201871

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