

In The Classroom

# Use of the Murnaghan-Hildebrand Equation of State in Teaching Thermodynamics

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*The purpose of this paper is to present the Murnaghan-Hildebrand equation of state for solids and liquids and to show at least some of the ways it can be used to illustrate basic thermodynamic relationships.*

The Murnaghan-Hildebrand equation of state, an accurate equation of state for many solids and liquids, is introduced for use in the illustration of thermodynamic relationships. It is shown to meet the need for an equation of state accurate over a wide range of pressures. Parameters are given for four solid phases of iron and for the liquid, with which eleven thermodynamic functions including  $V$ ,  $U$ ,  $H$ ,  $S$ ,  $\alpha V$ ,  $V/B$ , and  $G$  can be calculated at any specified temperature and pressure. The program for these calculations can be used to represent experimental values, to illustrate thermodynamic relationships, to calculate chemical and phase equilibria, and to stimulate student interest from the study of real systems, for instance, the form of iron in the core of the earth.

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## Introduction

The standard thermodynamic variables are complex functions of temperature, pressure, and composition. Fortunately, their derivatives are interrelated by expressions like the Maxwell

equations. For example:

$$\left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P \quad (1)$$

It is not intuitively obvious how useful partial derivatives can be; thus, it is important to give students a lot of experience using these equations. One way to accomplish this is by using an equation of state, which gives the volume of a pure material as a function of temperature and pressure:

$$V = f(T, P) \quad (2)$$

A good equation of state for student use should be both simple and accurate. The ideal gas equation of state is simple enough, but it yields trivial expressions like:

$$\left(\frac{dU}{dP}\right)_T = \frac{PV}{B} - \alpha VT = 0 \quad (3)$$

One can use the van der Waals equation of state to illustrate thermodynamic relationships as in a recent textbook [1]; however, I have found that none of the common equations of state for gases is accurate enough over a reasonably wide range of pressures to warrant a large investment in student time.

The situation is quite different for condensed phases. Nearly everyone in this subdiscipline uses the Murnaghan logarithmic equation of state to represent experimental data, and a simple extension of this equation, a Murnaghan-Hildebrand equation of state, works extremely well for many common materials including MgO [2] and iron [3]. The purpose of this paper is to present the Murnaghan-Hildebrand equation of state for solids and liquids and to show at least some of the ways it can be used to illustrate basic thermodynamic relationships.

### The Murnaghan Logarithmic Equation of State

The compressibility of any material, defined as

$$\beta = -\frac{1}{V}\left(\frac{dU}{dP}\right)_T \quad (4)$$

decreases with increasing pressure toward a limit of 0. It turns out to be very convenient to use the reciprocal of compressibility, which is called the bulk modulus and represented by the capital letter  $B$ .

$$B = -V \left( \frac{dP}{dV} \right)_T \quad (5)$$

For many materials  $B$  increases linearly with pressure:

$$B = B_0 + NP = -V \left( \frac{dP}{dV} \right)_T \quad (6)$$

where the subscript in  $B_0$  designates the value at zero pressure and  $N$  is a constant independent of pressure.  $N$  has no units because the bulk modulus has the same units as pressure. The last part of equation 6 can be integrated to give

$$V = V_0(1 + NP / B_0)^{-1/N} \quad (7)$$

where  $V_0$  is the volume at zero pressure.

There are three ways to show students that equations 5, 6, and 7 are consistent. Integration will demonstrate that you are a mathematical expert. Differentiating equation 7 is a procedure the best college students can follow. The third way, calculations for selected pressures, is the most convincing for the most students. For example, for iron at 298.15 K we have  $V_0 = 7.09085 \text{ cm}^3 \text{ mol}^{-1}$ ,  $B_0 = 168,681.17 \text{ MPa}$ , and  $N = 5$ . We can calculate the volume of alpha iron at 298.15 K and three pressures: 9,990; 10,000; and 10,010 MPa. This gives  $V_{9,990} = 6.732389028$ ,  $V_{10,000} = 6.732081137$ , and  $V_{10,010} = 6.73177333$ . We can then write:

$$\frac{\Delta V}{\Delta P} = \frac{-0.00061570}{20} = -3.0785 \times 10^{-5} \quad (8)$$

$$= \frac{-V}{B} = \frac{-6.732081137}{168681.17 + 50000} = 3.07849 \times 10^{-5} \quad (9)$$

Note that for checking equations involving derivatives and computer programming one must suspend the ordinary rules about significant figures. We get five significant figures in  $\Delta V/\Delta P$  only by using 9 or 10 decimal places in the values of  $V$ .

The calculations in equations 8 and 9 demonstrate a number of relationships, but particularly that volumes from equation 7 are consistent with the bulk modulus of equation 6.

### Hildebrand Equations of State

For a Hildebrand equation of state [4, 5], the pressure is equal to the pressure at that volume at 0 K plus a thermal pressure,  $P_{th}$ , independent of volume:

$$P = P_0(V, 0K) + P_{th}(T) \quad (10)$$

This can be valid for many expressions for volume as a function of pressure, but if equation 8 is used along with equation 10, one has a Murnaghan-Hildebrand equation of state.

### The Murnaghan-Hildebrand Equation of State

We can show two important consequences of a Murnaghan-Hildebrand equation of state by taking the derivative of equation 10 with respect to volume at constant temperature:

$$\left(\frac{dP}{dV}\right)_T = \frac{-B}{V} = \left(\frac{dP_0}{dV}\right)_{0K} + 0 \quad (11)$$

$$\frac{-B}{V} = -\frac{B_{0T} + NP}{V} = -\frac{B_{0K}}{V} = -\frac{B_{0, 0K} + N_0P}{V} \quad (12)$$

Equation 12 requires that  $N$  is independent of temperature as well as independent of pressure because  $N$  must equal  $N_0$ , the value at 0 K. Similarly, the bulk modulus must be the same function of volume at all temperatures, and in fact

$$B_T = B_{0, 0K} \left(\frac{V_{0, 0K}}{V_T}\right)^N \quad (13)$$

or more usefully

$$B_T = B_0^* \left( \frac{V_0^*}{V_T} \right)^N \quad (14)$$

because  $V_0$  and  $B_0$  are more commonly known at a standard temperature like 298.15 K (designated by the asterisk subscript) than at 0 K. Thus equation 7 is a Murnaghan-Hildebrand equation of state if equation 14 holds as well.

Equation 14 is extremely useful because it supplies values for the bulk modulus for temperatures at which it has not been measured. It was initially derived [2] by a double integration on the assumption that  $N$  was constant, independent of temperature and pressure. However, we have omitted a constant of integration, and equation 14 holds only for materials following the Murnaghan-Hildebrand equation of state. It does not work for liquid water even if  $N$  is independent of temperature. The easy way to get equation 14 is by solving equation 7 for  $B = B_0 + NP$ . That shows  $B$  as a function of  $V$  at constant temperature, and  $B$  will be the same function of  $V$  at all temperatures if the substance follows a Hildebrand equation of state, with a thermal pressure which is a function of temperature only.

### Applications to Real Materials

Equations 6, 7, and 14 can be used to calculate the thermodynamic properties of a material at any temperature and pressure provided they are known at some standard temperature and pressure, normally 298.15 K and 0.1000 MPa.  $C_p$  and  $V$  must be known as functions of temperature at low pressure, but this information is generally available for any common material. At least one value of the bulk modulus must be known. The value of  $N$  can often be estimated with reasonable accuracy, or it can be calculated from two values of the bulk modulus using equation 6 or 14. The only assumption required is that the material follows a Murnaghan-Hildebrand equation of state. This assumption appears to be reasonable for most solids and liquids, excluding those like liquid water and alpha quartz which have peculiar coefficients of thermal expansion.

A recent paper [2] showed that MgO(c) data was well fitted by a Murnaghan-Hildebrand equation of state. The single value,  $N = 4.57$ , fits both the pressure and

temperature dependence of the bulk modulus. Solid sodium chloride is a more compressible solid, which has been proposed as a pressure calibration standard [6]. The tabulated volume data for sodium chloride from a complex Birch-Murnaghan equation of state [6] are well represented by  $B_0^* = 24.1$  GPa and  $N = 4.4$  from 273 to 1073 K and pressures up to 10.6 GPa. Even wider ranges of temperature and pressure are covered accurately by Murnaghan-Hildebrand equations of state for liquid iron and various iron crystal structures. Data are available for hexagonal closed packing for iron from 13 to 301 GPa at room temperature [7]. Any constant value for  $N$  between 4 and 5 will do a good job of fitting the volume data over this wide pressure range. Murnaghan-Hildebrand equations of state are also adequate for fitting the experimental data for solid gold, another material which has been proposed [8] for pressure calibration at high temperatures. One can reasonably expect it to hold for the chemicals involved in life processes at least to the pressures found in the ocean depths.

Evaluating  $N$  from volume data using equation 6 or 14 really involves a second derivative, so small changes in  $N$  may not be noticeable; however, more accurate bulk modulus values can be obtained from ultrasonic velocities or direct measurement of elastic constants. Such measurements on San Carlos olivine [9] are accurately fitted by the linear expression

$$B = 126.3 + 4.28P \quad (15)$$

Of course one can find other solids, like Kilbourne hole orthopyroxene [10] where a quadratic is indicated. In fact, many materials including liquid water and liquid mercury have a value for  $(dB/dP)_T$  well above 5.0. For gases at high pressure, high values of  $N$  are required for the bulk modulus to increase from the value zero at the critical point to values similar to solid and liquid values. In all these cases the values of  $N$  vary with pressure, decreasing as pressure increases. A so called universal equation of state has been proposed [11, 12] with this feature. However for teaching purposes it is important to choose a simple model, and counterproductive to dwell on its limitations. The Murnaghan-Hildebrand equation of state works, often within the accuracy of the experimental data.

### Using the Murnaghan-Hildebrand Equation

Equation 1 provides an accurate expression for the pressure dependence of entropy. It

can be checked by calculating entropy and volume at four points around a particular temperature and pressure. Thus, the entropy of epsilon ( $\epsilon$ ) iron at 800 K and 13,995 MPa is 53.632030 J mol<sup>-1</sup> K<sup>-1</sup>, decreasing to 53.628964 J mol<sup>-1</sup> K<sup>-1</sup> when the pressure is increased to 14,005 MPa. Thus,  $\Delta S/\Delta P = -0.003066/10$ . This is approximately equal to  $(dS/dP)_T$  which agrees with the value for  $\alpha V$  at 800 K and 14,000 MPa, 0.000306562 cm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>. We can also show that  $(dV/dT)_P = \alpha V$  by calculating the volume at 14,000 MPa and the two temperatures, 795 and 805 K: (6.462471–6.459406)/10 = 0.003065.

When the equation of state is known for any material, we can calculate the quantity  $\alpha V$  at any temperature and pressure we choose. Because  $V$  is a state function, the two ways of taking a mixed second derivative must be equal. Thus we have:

$$\frac{d^2V}{dPdT} = \left( \frac{d(\alpha V)}{dP} \right)_T = \left( \frac{d\left(\frac{-V}{B}\right)}{dT} \right)_P \quad (16)$$

and explicitly taking the last derivative

$$\left( \frac{d\left(\frac{-V}{B}\right)}{dT} \right)_P = \left( \frac{-\alpha V}{B} \right)_P + \left( \frac{V}{B^2} \right) \left( \frac{dB}{dT} \right)_P \quad (17)$$

and equation 14 can be used to evaluate  $(dB/dT)_P$ . It is not essential that students trust or even follow the derivation of these formulas. They should be able to take calculated values at the four temperature and pressure pairs above and show that

$$\frac{\Delta(\alpha V)}{\Delta P} = \frac{\Delta\left(\frac{V}{B}\right)}{\Delta T} \quad (18)$$

The Murnaghan-Hildebrand equation of state is simple enough that integrations of  $(d(\alpha V)/dP)_T$  and even  $(dC_p/dP)_T$  can be performed analytically, but this skill is almost unnecessary in the modern computer age. The required integrals over temperature and pressure can be put into suitable computer programs, and a full set of

**TABLE 1.** Thermodynamic Values For  $\epsilon$  Iron at Temperatures and Pressures Near 800 K and 14000 MPa.

Quality								Units
T	800.0000	800.0000	800.0000	795.0000	800.0000	80500000	800.1000	K
P	13995.00	14000.00	14005.00	14000.00	14000.00	14000.00	14007.626	MPa
V	6.461086	6.460939	6.460792	6.459406	6.460939	6.462471	6.460746	cm <sup>3</sup> mol <sup>-1</sup>
U	18870.49	18871.32	18872.15	18738.07	18871.32	19004.81	18875.25	J mol <sup>-1</sup>
H	109293.4	109324.5	109355.5	109169.7	109324.5	109479.4	109375.0	J mol <sup>-1</sup>
S	53.63203	53.63050	53.62896	53.43649	53.63050	53.82357	53.63203	J mol <sup>-1</sup> K <sup>-1</sup>
A	-24035.1	-24033.1	-24031.0	-23743.9	-24033.1	-24323.2	-24035.7	J mol <sup>-1</sup>
G	66387.76	66420.07	66452.37	66687.74	66420.07	66151.43	66463.98	J mol <sup>-1</sup>
Y	-76.0977	-76.1381	-76.1785	-76.9536	-76.1381	-75.3315	-76.1834	J mol <sup>-1</sup> K <sup>-1</sup>
PV	90422.90	90453.15	90483.39	90431.68	90453.15	90474.60	90499.71	J mol <sup>-1</sup>
$\alpha V$	0.000307	0.000307	0.000307	0.000307	0.000307	0.000306	0.000306	cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup>
V/B	0.000029	0.000029	0.000029	0.000029	0.000029	0.000029	0.000029	cm <sup>3</sup> /(mol MPa)
C <sub>p</sub>	30.96572	30.96588	30.96604	30.92191	30.96588	31.00985	30.96701	J mol <sup>-1</sup> K <sup>-1</sup>
V/B	0.029363	0.029359	0.029355	0.029318	0.029359	0.029401	0.029354	cm <sup>3</sup> /(mol GPa)
H <sub>0</sub>	5509.600	5509.600	5509.600	5509.600	5509.600	5509.600	5509.600	J mol <sup>-1</sup>
C <sub>v</sub>	28.40455	28.40507	28.40558	28.37009	28.40507	28.44011	28.40655	J mol <sup>-1</sup> K <sup>-1</sup>
H-H <sub>0</sub>	103783.8	103814.9	103845.9	103660.1	103814.9	103969.8	103865.4	J mol <sup>-1</sup>
Np <sup>a</sup>	0.000801	0.000800	0.000800	0.000798	0.000800	0.000803	0.000800	cm <sup>3</sup> mol <sup>-1</sup> GPa <sup>-2</sup>
$\alpha$	47.45388	47.44849	47.44310	47.49127	47.44849	47.40574	47.43942	MK <sup>-1</sup>
B	220038.1	220063.1	220088.1	220324.4	220063.1	219802.3	220096.0	MPa
B <sub>s</sub>	239878.3	239902.5	239926.7	240142.0	239902.5	239662.8	239934.6	MPa
N	5.000000	5.000000	5.000000	5.000000	5.000000	5.000000	5.000000	

a) The quantity Np is  $(1+N)*V/B^2$  in units of cm<sup>3</sup> mol<sup>-1</sup> GPa<sup>-2</sup>



11 thermodynamic functions can be calculated at specified temperatures and pressures for any material for which one has a suitable data file of input parameters. Table 1 shows such calculated values for seven combinations of  $T$  and  $P$  near 800 K and 14,000 MPa for epsilon iron.

With the values in Table 1 it is easy to show that both sides of equation 18 are equal to  $-8.4 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1} \text{ K}^{-1}$ . It is often useful to check derivations and programming by calculations of  $\Delta Q/\Delta X$  for a real substance, where  $Q$  and  $X$  can be any thermodynamic variable. Table 2 shows 20 partial derivatives of the form  $(dQ/dP)_T$  or  $(dQ/dT)_P$  which can be checked in this way.

One can also use Table 2 to derive general partial derivatives where something other than temperature or pressure is held constant. For example, to evaluate  $(dV/dP)_S$ , which equals  $-V/B_S$ , one writes three equations, setting the third to zero:

$$dV = -\left(\frac{V}{B}\right)dP + (\alpha V)dT \quad (19)$$

$$dP = 1dP + 0 \quad (20)$$

$$dS = -(\alpha V)dP + \left(\frac{C_p}{T}\right)dT = 0 \quad (21)$$

Solving equation 21 for  $dT$  and substituting this into the other equations to get  $dV$  and  $dP$  gives

$$\left(\frac{dV}{dP}\right)_S = -\frac{V}{B} + \frac{(\alpha V)^2 T}{C_p} = -\frac{V}{B_S} \quad (22)$$

which is the correct relationship between the bulk modulus at constant temperature and the isoentropic bulk modulus,  $B_S$ .

Care has been taken in Table 2 and equation 22 to keep the quantities  $(\alpha V)$  and  $(V/B)$  together, because they must stay together in calculating changes in chemical reactions and in equations for partial molal quantities. Thus,

**TABLE 2.** Partial derivatives of 11 extensive thermodynamic quantities with respect to temperature and pressure.

Quantity	Partial Derivatives	
Q	$(dQ/dP)_T$	$(dQ/dT)_p$
T	0	1
P	1	0
V	$-V/B$	$\alpha V$
U	$PV/B - T\alpha V$	$C_p - P\alpha V$
H	$V - T\alpha V$	$C_p$
S	$-\alpha V$	$C_p/T$
A	$PV/B$	$S - P\alpha V$
G	$V$	$-S$
Y <sup>a</sup>	$-V/T$	$(H-H(298\text{ K}))/T^2$
PV	$V - PV/B$	$P\alpha V$
$\alpha V$	$-d(V/B)/dT - (V/B)(\alpha V)(1+N)/V$ <sup>b</sup>	$d(\alpha V)/dT$
V/K	$-d^2V/dP^2 - (V/B)^2(1+N)/V$ <sup>b</sup>	$d(V/B)/dT(V/B)(\alpha V)(1+N)/V$ <sup>b</sup>
$C_p$	$-(1/T)(d(\alpha V)/dT)$	$dC_p/dT$

a) The Planck function, Y, is defined as  $-(G-H(298\text{ K}))/T$

b) Values taken for complex derivatives if the substance follows a Murnaghan-Hildebrand equation of state.

$$\left(\frac{d\Delta V}{dT}\right)_p = \Delta(\alpha V) \quad (23)$$

and the derivative is not equal to  $\Delta\alpha^*\Delta V$ . Similarly, while the dimensionless quantity,  $N$ , plays the major role in the Murnaghan-Hildebrand equation of state, it is the complex combinations shown in Table 2,  $(V/B)^2(1+N)/V$  and  $(V/B)(\alpha V)(1+N)/V$ , which are second derivatives of  $V$  and thus are well behaved thermodynamically. The output of the thermodynamic program, PHF, includes a number of values like  $\alpha$ ,  $B$ ,  $B_s$ , and  $N$ , which are not linear functions of the extensive thermodynamic parameters. They are included at the bottom of Table 1, but it is important to recognize that

changes in these quantities cannot automatically be substituted into the standard thermodynamic equations.

The procedure used in equations 19 through 22 is applicable to get expressions for any thermodynamic relationship involving the 13 parameters in the table. A good test of student understanding of the process is to use the expressions for  $dU$ ,  $dT$ , and  $dV$  to derive the relationship

$$\left(\frac{dU}{dT}\right)_v = C_p - T(\alpha V)^2 \frac{B}{V} \quad (24)$$

One involving even more cancellation of terms is to show that  $(dU/dV)_S = P$ .

### Calculations with the Program PHF

It is possible to check relationships like equation 22 with a computer program as well. The program PHF is designed for calculations at a particular temperature, with pressure as the next input value. If you want calculated values at a particular volume or entropy, a trial and error procedure is required. Thus, the first step in calculating a column like number 8 in Table 1 is to pick a temperature. For this example, we pick 800.1 K. The next step is to pick pressures until you bracket the value wanted. For column 8 we want an entropy of  $53.632030 \text{ J mol}^{-1} \text{ K}^{-1}$ , which requires a pressure between 14010 and 14000 MPa. Then, four pressures are tested to narrow the range to between 14,007 and 14,008. One can use an interpolation procedure to pick the next pressure value to try, but the computer calculation is so fast that it is just as efficient to try three or four values as one moves to the next decimal place. In any case, the final pressure needed to match the sixth decimal place in  $S$  is 14,007.626 MPa. Using columns 2 and 8 of Table 1, it can be shown that

$$B_S = V \left( \frac{\Delta P}{\Delta V} \right) = 6.461 \left( \frac{12.626}{0.000340} \right) = 239,931 \text{ MPa} \quad (25)$$

which agrees with Table 1 values to four significant figures.

### Values for Iron

All of the values in Table 1 are for epsilon iron, the hexagonal closest-packed crystal,

which is thermodynamically stable at this temperature and pressure. It is generally stable at low temperatures and pressures above 13,000 MPa. The cubic-closest-packed structure, gamma ( $\gamma$ ) iron, also has a substantial region of thermodynamic stability, and it is possible to calculate its thermodynamic properties at 800 K and 14,000 MPa. Its free energy, defined by the two equations:

$$G = H - TS \quad (26)$$

$$H = \Delta_f H(298 \text{ K}, 0.1 \text{ MPa}) + (H - H(298 \text{ K})) \quad (27)$$

is  $66,638.61 \text{ J mol}^{-1} \text{ K}^{-1}$ , only slightly more than that of the epsilon crystals at this temperature and pressure,  $66,420.07 \text{ J mol}^{-1} \text{ K}^{-1}$ . It is very convenient to have the option of output from the program PHF as columns of values in a standard order as in Tables 1 and 3, ready for input into a spreadsheet program, so that with the effort to calculate  $\Delta G = 218.54 \text{ J mol}^{-1}$  we can also get values for  $\Delta V$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , etc. as shown in column 6 of Table 3. The value of  $\Delta S = 4.0036 \text{ J mol}^{-1} \text{ K}^{-1}$  indicates that the two phases will be in equilibrium at a temperature about 55 K higher. Columns 3, 5, and 7 of Table 3 show that the two phases have equal free energy at 854.56 K and 14,000 MPa. Similarly the equilibrium temperature can be found for other pressures.

If we have measured values or estimates for the thermodynamic values for the body centered cubic phase and for liquid iron, and we assume that Murnaghan-Hildebrand equations of state are suitable at least over a range of pressures, it is possible to calculate a full phase diagram for iron as in Figure 1. This merely involves repeating calculations like that described in the previous paragraph for many pressures and several pairs of forms of iron.

### Input Data for the PHF Program

As input for thermodynamic calculations one needs a set of thermodynamic variables at 298.15 K and 0.1000 MPa, the selected standard temperature and pressure. The standard values we choose in designing input files are  $S$ ,  $H$ ,  $C_p$ ,  $V$ ,  $V/B$ ,  $(V/B)^2$ ,  $(1 + N)/V$ , and  $\alpha V$ . One also needs equations for the temperature dependence of  $C_p$  and of  $V$  at the standard pressure, or any other low pressure. These are represented by the two equations:

**TABLE 3.** Thermodynamic Values For  $\epsilon$  Iron at Temperatures and Pressures Near 800 K and 14000 MPa.

Quality	Fe		D-B		E-C	
T	800	854.56	800	854.56	800	854.56
P	14000	14000	14000	14000	14000	14000
V	6.46094	6.4776	6.5471	6.56457	0.08616	0.08697
U	18871.3	20340.6	21086.5	22547.5	2215.18	2206.9
H	109324	111027	112745	114451	3421.43	3424.44
S	53.6305	55.6891	57.6341	59.6964	4.00362	4.00725
A	-24033.1	-27249.1	-25020.8	-28466.6	-987.707	-1217.54
G	66420.1	63437.4	66638.6	63437.4	218.538	0.00133
Y	-76.1381	-67.7866	-73.5859	-65.1416	2.55222	2.645
PV	90453.1	90686.5	91659.4	91904	1206.25	1217.54
$\alpha V$	0.00031	0.0003	0.00032	0.00032	$1.5 \times 10^{-5}$	$1.5 \times 10^{-5}$
V/B	$2.9 \times 10^{-5}$	$3 \times 10^{-5}$	$3.1 \times 10^{-5}$	$3.2 \times 10^{-5}$	$2 \times 10^{-6}$	$2 \times 10^{-6}$
CP	30.9659	31.4457	31.0192	31.5028	0.05331	0.05705
$V \times 10^3/B$	0.02936	0.02982	0.03104	0.03154	0.00168	0.00173
H (298 K)	5509.6	5509.6	7769.91	7769.91	2260.31	2260.31
$C_v$	28.4051	28.7911	28.3552	28.7468	-0.04987	-0.04433
H-H (298 K)	103815	105517	104976	106682	1161.12	1164.13
$N_p \times 10^6$	0.0008	0.00082	0.00088	0.00091	$8.3 \times 10^{-5}$	$8.6 \times 10^{-5}$
$a \times 10^6$	47.4485	46.9832	49.1086	48.5865	1.66016	1.60331
B	220063	217247	210901	208109	-9162.16	-9137.55
$B_s$	239902	237277	230715	228061	-9187.26	-9216.57
N	5	5	4.99999	4.99999	$-7 \times 10^{-6}$	$-7 \times 10^{-6}$

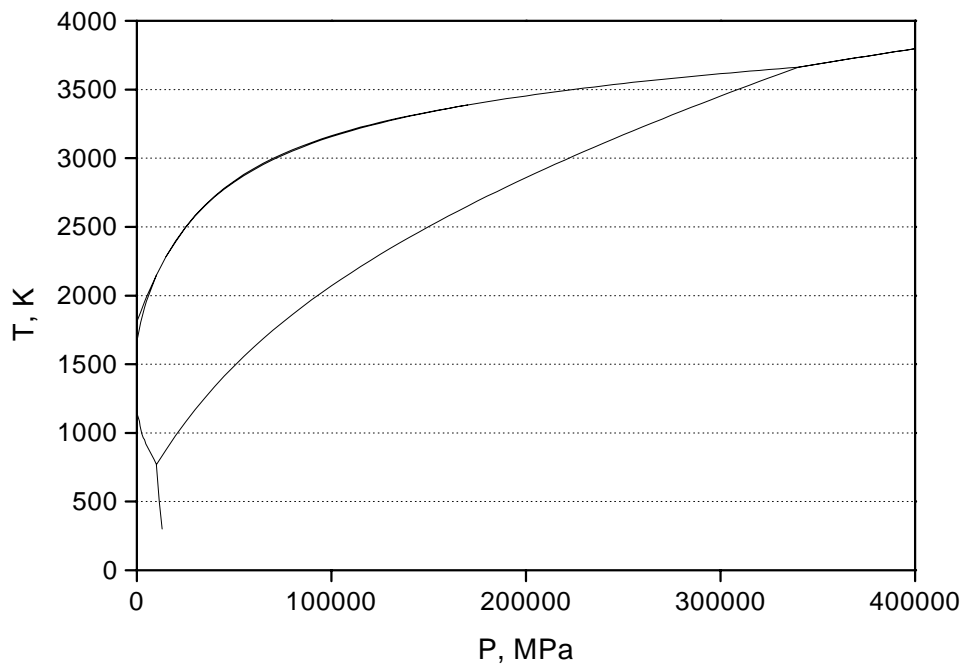


FIGURE 1. CALCULATED PHASE DIAGRAM FOR IRON.

**TABLE 4.** The form used for input files for the program PHF.

Chemical formula and form  
 Reference  
 More Reference data  
 Temperature range, pressure range  
 Person compiling the data  
 Original data and the date of the last revision

S	L <sup>a</sup>	H		
C <sub>p</sub>	A	B	C	D
E	F			
V	V/B	(V/B) <sup>2</sup> (1-N)/V TαV		M <sup>b</sup>
αV	H	I	J	K

a) A value other than 0.0 is required for L only if the heat capacity equation is not valid at 298.15.

b) A value of M = 0.0 is used for all materials which follow a Murnaghan-Hildebrand equation of state. It is included in the program to allow calculations for other materials, like H<sub>2</sub>O (l).

$$C_p = C_p(298.15 \text{ K}, 0.1 \text{ MPa}) + A(T - 298.15) + B(T - 298.15)^2 + C(T - 298.15)^3 + D(T - 298.15)^4 + E(T^{-0.5} - 298.15^{-0.5}) + F(T^{-2} - 298.15^{-2}) \quad (28)$$

$$V = V(298.15 \text{ K}, 0.1 \text{ MPa}) + \alpha V(T - 298.15) + H(T - 298.15)^2 + I(T - 298.15)^3 + J(T - 298.15)^4 + K(T - 298.15)^5 \quad (29)$$

Even with seven terms in the power series for  $C_p$ , the equation is adequate over only a limited range of temperatures. When the valid temperature range does not include 298.15 K, one needs a correction value for enthalpy which is represented in Table 4 by the letter L. Eleven lines of input are used for each chemical substance. The first line describes the material and form and the next five lines show references, range of validity, etc., important data but not used in the computer calculations. The input values are arranged on the next five lines as shown in Table 4. Values for three low-temperature crystal forms of iron are shown in this format in Table 5, and values for higher temperatures and for liquid iron are in Table 6.

It is usually possible to find all of the values at 298.15 K and 0.1000 MPa needed as input for a material. Estimates are often adequate for missing values. For example the heat capacity for  $\epsilon$  iron is estimated from that for  $\gamma$  iron, and values of  $N$  in the range from 4 to 5 fit many substances. It is a bit awkward to require one to calculate  $(V/B)^2 (1 + N)/V$  for input in place of  $N$ , but this inconvenience is more than repaid in having a value that works consistently in calculations of changes in chemical reactions or partial molal quantities.

The relationships in Table 2 and output like that in Tables 1 and 3 can be used for a wide variety of student problems for homework or exams. The file SUPP23.TXI gives some simple examples in the form of a cooperative education assignment formulated for a seminar in which this material was presented.

**TABLE 5.** Values for Three Low-Temperature Crystal Forms of Iron.

```
Fe (c, epsilon, hcp)
for gamma-liquid-epsilon equilibria
H.-K. Mao, W. A. Bassett, and T. Takahashi, J. appl. Phys., 38, 272 (1967)
1500-4000K, 0-1000 MPa
Reed A. Howald
8/12/96, 8/12/96
31.146 0.00 5509.6
26.453512 0.008403 -1.7411e-8 0. 0.
0. 0.
6.73153 37.5541e-6 0.001257049 0.
4.8534e-4 0. 0. 0. 0.
Fe (l)
from EQFEH.DAT of5/19/88
V and alpha*V to fit melting data at high P
1500-4000K, 0-1000 MPa
Reed A. Howald
8/12/96, 9/18/96
31.7326783 -2527.98 10144.85
41.418524 .0016736 0.0 0.0 0.0
0. 0.
6.8511 40.6416e-6 0.00144655 0.
7.31875e-4 0. 0. 0. 0.
Fe(c,gamma,fcc)
from FENIC of autumn 1976, K to fit equil. with liquid
Z. E. Basensky, W. Hume-Rothery, and Sutton, Proc. Roy. Soc., 229, 459 (1955)
290-4000K, 0-3000 MPa
Reed A. Howald
8/12/96, 9/29/96
35.4754 0.00 7769.913
26.45589 0.0084014 -1.7411e-8 0. 0.
0. 0.
6.83531 40.2e-6 0.00141855 0.
5.2168e-4 0. 0. 0. 0.
Fe (c, delta, bcc, T>1274)
from EQFEH.DAT of5/19/88
adjusted to equil. with gamma at 1665 K, delta H = 815 J
1274-2050K, 0-2000000 MPa
Reed A. Howald
8/12/96, 9/30/96
43.0942846 -14861.196 0.00
80.247604 -0.0881192 0.604944e-4 -0.130918e-7 0.
0. 0.
6.88916 35.3568e-6 0.00108876 0.00
5.12810e-4 0.0 0.0 0.0 0.
Fe (c,alpha, bcc, low T)
least squares to JANAF 1988 values
alpha from Touloukian
200-900 K, 0-2000 MPa
Reed A. Howald
8/12/96, 9/30/96
27.280 0.00 0.00
24.981604514 0.02923819825 -.41368922566e-4 6.55304271976e-8 8.891928082666e-12
0. 0.
7.09085 42.037e-6 0.00149526 0.
2.93975e-4 2.25559e-8 0. 0. 0.
```



**TABLE 6.** Values for Higher-Temperature Crystal Forms of Iron and for Liquid Iron.

```

Fe (c, epsilon, hcp)
for gamma-liquid-epsilon equilibria
H.-K. Mao, W. A. Bassett, and T. Takahashi, J. appl. Phys., 38, 272 (1967)
2050-6000K, 0-1000 GPa
Reed A. Howald
8/12/96, 10/5/96
48.112286 -8840.735 5509.6
36.56519 0.0026 0.00 0. 0.
0. 0.
6.73153 37.5541e-6 0.00125705 0.
4.8534e-4 0. 0. 0. 0.
Fe (l)
from EQFEH.DAT of 5/19/88
V and alpha*V to fit melting data at high P
1500-6000K, 0-1,000,000 MPa
Reed A. Howald
8/12/96, 9/18/96
31.7326783 -2527.980 10144.85
41.418524 .0016736 0.0 0.0 0.0
0. 0.
6.8511 40.6416e-6 0.00144655 0.
7.31875e-4 0. 0. 0. 0.
Fe(c,gamma,fcc)
from FENIC of autumn 1976 via EQFEH.DAT of 5/19/88 Z. S. Basinsky,
W. Hume-Rothery, and A. L. Sutton, Proc. Roy. Soc. A, 229, 459 (1955)
2050-6000K, 0-100000 MPa
Reed A. Howald
8/12/96, 10/5/96
52.438562 -8838.995 7769.913
36.56519 0.0026 0.00 0. 0.
0. 0.
6.83531 40.2e-6 0.00141855 0.
5.2168e-4 0. 0. 0. 0.
Fe (c, delta A, bcc, T>2050)
volume Basensky 1955, K Mao 1967
adjusted to equil. with gamma at 1665 K, delta H = 815 J
2050-6000K, 0-1,000,000 MPa
Reed A. Howald
8/12/96, 1/9/97
23.3022606 43.333 0.00
36.56519 0.0026 0.00 0.00 0.
0. 0.
6.88916 0.0000420152 0.00153744 0.
5.1281e-4 0.0 0.0 0.0 0.

```

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## REFERENCES

1. Roy, B. N. *Principles of Modern Thermodynamics*; IOP Publishing: Philadelphia, PA, 1995.
2. Howald, R. A.; Jones, R. D.; Rezvani, A. B.; Roy, B. N.; Scanlon, M. J.; Swager, T. M. *J. Phys. Chem.* **1985**, *89*, 2682.
3. Howald, 1997; See the file IRON5.TXH in 32RH2897.
4. Hildebrand, J. H. Gitterenergien vom thermodynamischen Standpunkt aus, *Zeitschrift für Physik* **1931**, *67*, 127.
5. Huang, K. *Philos. Mag.* **1951**, *42*, 202.
6. Decker, D. L. *J. Appl. Phys.* **1971**, *42*, 3239.
7. Mao, H.-K.; Bassett, W. A.; Takahashi, T. *J. Appl. Phys.* **1990**, *38*, 272.
8. Ming, L. C.; Manghnani, M. H.; Balogh, J. Qadri, S. B.; Skelton, E. F.; Jamieson, J. C *J. of Appl. Phys.* **1983**, *54*, 4390
9. Abramson, E. H.; Brown, J. M.; Slutsky, L. J.; Zaug, J. *J. Geophys. Res.* **1997**, *102B*, 12253.
10. Chai, Mu.; Brown, J. M.; Slutsky, L. J. **1997**, *102B*, 14779.
11. Vinet, P.; Ferrante, J. Rose, J. H.; Smith, J. R. *J. of Geophys. Res.* **1987**, *92B*, 9319.
12. Vinet, P.; Smith, J. R.; Ferrante, J.; Rose, J. H. *Phys. Rev. B, Condens. Matter* **1987**, *35B*, 1945.