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Calculated Enthalpies of Transition at 0 K for Several Metallic Phase Transition

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ABSTRACT

Enthalpy differences at 0 K and 1 atm have been estimated for the transitions bcc Fe ⇌ hcp Fe, rhombohedral Hg ⇌ bct Hg, bcc Ba ⇌ hcp Ba, and bcc Cs ⇌ fcc Cs. The values of ΔH₀ are, respectively, +1.07±.13, −.03±.02, +.66±.05, and 1.0±.7 kcal/mole.
The enthalpy difference at 0 K and 1 atm for a pressure-induced crystal phase transformation at some non-zero temperature from a structure stable at low pressure (LP) to one stable at high pressure (HP) can be estimated if sufficient experimental data is available. Values of $\Delta H^0$ for the transitions bcc Fe $\rightarrow$ hcp Fe, rhombohedral Hg $\rightarrow$ bct Hg, bcc Cs $\rightarrow$ fcc Cs, and bcc Ba $\rightarrow$ hcp Ba have been calculated and are presented in Tables I-IV. Brewer\textsuperscript{1} has used these values to calculate $\Delta H^0$ for the atomization of the HP phases under consideration.

For the process $m^{LP}$ (0 K, 1 atm) $\rightarrow$ $m^{HP}$ (0 K, 1 atm)

$$\Delta H^0 = \int_{0}^{T^*} c_P^{LP} dT + \int_{1}^{P^*} V^{LP} dP - T^* \int_{1}^{P^*} \left( \frac{\partial V}{\partial T} \right)_P dP + H_{T^*} + T^* \int_{1}^{P^*} \left( \frac{\partial V}{\partial T} \right)_P dP - \int_{1}^{P^*} V^{HP} dP - \int_{0}^{P^*} c_P^{HP} dT$$

(A) (B) (C) (D) (E) (F) (G)

since $\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$. Physically, this represents the warming of the LP form at 1 atm to some temperature $T^*$ at which a reversible transformation can occur, isothermal compression of the LP form to the corresponding transformation pressure $P^*$, transformation to the HP form, and the hypothetical isothermal decompression followed by isobaric cooling of the HP form to 0 K and 1 atm. The letters below the terms of the equation are used for identification in the Tables.

The enthalpy of transformation $T^*$ and $P^*$, $\Delta H_{T^*}$, was calculated using the Clapeyron equation, $dP/dT = H/T\Delta V$, where $dP/dT$ is the change in transformation pressure with temperature, and $\Delta V$ the change in molal volume.

Terms B and F for isothermal compression at $T^*$ are large and somewhat uncertain because of experimental difficulty and the instability of HP phases below transition pressures. Cannon\textsuperscript{2} has critically reviewed high pressure studies of the elements, and his conclusions have been accepted
where experimental results vary.

Compressibility measurements have been made\(^3\) on metastable hcp Fe below \(P^*\). The volume of bct Hg was calculated as a function of \(P\) at 152 K using Swenson's\(^4\) values of \(\frac{3V}{RT}/P\) and of \(V\) for the 180 K isotherm.

Volumes for fcc Cs and hcp Ba have been measured only at \(P > P^*\). Molal volumes of LP phases at 1 atm, needed to convert compressibilities to volumes, were taken from Donohue.\(^5\)

Predicting the equation of state of a metal is an exceedingly complex problem, about which Bernardes and Swenson\(^6\) reviewed various approaches and listed references. Molal volumes predicted from the sparse experimental information have been used to estimate \(\Delta H_0^\circ\) in preference to strictly theoretical values. The procedure used for fcc Cs and hcp Ba was to estimate volumes by connecting values for volumes at \(P^*\) with an estimated volume at 1 atm as described below.

Wittenberg and DeWitt\(^7\) plotted the inverse viscosity \(n^{-1}\) of various metals against molal volume. The volume at \(n^{-1} = 0\) was found to closely approximate that of close packed structures. The viscosity\(^8\) and density\(^9\) of liquid Cs were used to predict a close packed volume at 1 atm of 68.4 cm\(^3\)/mole. No correction for thermal expansion was needed since \(n^{-1} = 0\) near 298 K.

Molal volumes were converted to Wigner-Seitz radii, \(r = (3V/4\pi N_o)^{\frac{1}{3}}\), where \(N_o = 6.022 \times 10^{23}\), and plotted versus pressure. The radii varied less rapidly than the volumes, which aided graphical manipulations. Royce\(^10\) has observed that approximate universal compression curves exist where metallic bonding is governed by the same electron orbitals. The curves of \(r\) versus \(P\) for fcc Cs and hcp Ba should resemble those of the
bcc phases shifted on the pressure axis to agree with the known values of r at P \geq P^* . When this method was applied to fcc Cs, the value of r at 1 atm corresponded to 68.4 cm\(^3\)/mole as predicted. For hcp Ba the 1 atm value of the volume was 37.34 cm\(^3\). Although this value is only an estimate, the corresponding radius ratio \( r_{\text{bcc}} / r_{\text{hcp}} = 2.4754 / 2.4554 = 1.008 \) agrees with that for Cs, \( r_{\text{bcc}} / r_{\text{fcc}} = 3.0290 / 3.0043 = 1.008 \).

Volumes were fitted to equations of the form \( V = a + bP + cP^2 + dP^3 \) from which the integrals \( \int VdP \) were calculated.

Debye heat capacity functions \(^{11} \int c_VdT \) were used to approximate terms A and G. At the temperatures under consideration lattice contributions to enthalpy are dominant. Koskimaki and Waber\(^{12} \) estimated the lattice, electronic, and magnetic contributions to enthalpy for bcc and fcc Fe; at 300 K the two later account for 20 and 27 extra calories in bcc Fe. The electronic structure of hcp Fe predicted on the basis of the Engel-Brewer theory, \(^{1,13} d^6 \) sp, is intermediate between bcc Fe (d\(^6\) sp\(^0.5\)) and fcc Fe (d\(^5\) sp\(^1.5\)); therefore, 24 cal has been added to the 298 K enthalpy of hcp Fe. No correction was made for the other elements. The Debye temperatures used for LP phases were from Gray\(^{14} \) except for Fe, for which the value of Weiss and Tauer,\(^{15} 420 \) K, was used. Their analysis gave a value of \( \Theta_D = 335 \) K for fcc Fe. An intermediate value, 378 K, was used for the hcp form. Debye temperatures for the HP phases of Cs and Ba were estimated using the relationship \( \Theta_A = \Theta_B (V_B/V_A)^{\frac{1}{3}} (M_B/M_A)^{\frac{1}{2}} \), where V and M represent molal volume and weight. The weight ratio is included to allow the comparison of calculated and experimental values of \( \Theta_D \) shown in Table V.

The terms involving \( \frac{\partial V}{\partial T} \) have been evaluated from experimental values for the Hg polymorphs. For the other elements the third law of thermo-
dynamics and the relationship $\int dS = -\int \left(\frac{\partial V}{\partial T}\right)_p dP$ imply

$$\Delta S_0 = \int_0^{T_c} \frac{c_p}{T} dT - \int_1^{P_c} \left(\frac{\partial V}{\partial T}\right)_p dP + \frac{\Delta H^*_T}{T^*} + \int_1^{P_0} \left(\frac{\partial V}{\partial T}\right)_p dP - \int_0^{T^*_e} \frac{c_p}{T^*} dT = 0$$

from which

$$T^* \int_1^{P^*_e} \left(\frac{\partial V}{\partial T}\right)_p dP - T^* \int_1^{P^*_e} \left(\frac{\partial V}{\partial T}\right)_p dP = T^* \int_0^{T^*_e} \frac{c_p}{T} dT - T^* \int_0^{T^*_e} \frac{c_p}{T} dT - \Delta H^*_T.$$ 

The $\int \frac{c_p}{T} dT$ integrals were approximated by Debye functions. This procedure was reversed to predict $\theta_D$ for bct Hg.

Uncertainty in values of $\Delta H^*_0$ becomes larger as the amount and reliability of experimental data decreases. The uncertainty for Hg should not be greater than ±.02 kcal mole$^{-1}$. A negative value is indicated since the bct structure is stable at 1 atm below 79 K. The range of $P^*_e$ values reported for Fe leads to an uncertainty in $\Delta H^*_0$ of ±.13 kcal mole$^{-1}$. The estimated volumes of fcc Cs and hcp Ba are the greatest sources of error. A volume of 67.4 cm$^3$ mole$^{-1}$ for fcc Cs at 1 atm would increase $\Delta H^*_0$ by .05 kcal mole$^{-1}$, and a 0.5 cm$^3$ decrease in the estimated volume of hcp Ba at 1 atm would increase $\Delta H^*_0$ by .7 kcal mole$^{-1}$. The error limits assigned on this basis should thus be regarded as reasonable estimates.

Acknowledgments:

The author wishes to thank Professor Leo Brewer for his advice and encouragement. This work was supported by the U. S. Energy Research and Development Administration and the National Science Foundation, (Grant # MPS 73-04801-A01).
TABLE I

Evaluation of $H_0^\circ$ for Fe.

<table>
<thead>
<tr>
<th>Ref. 19</th>
<th>Ref. 3</th>
<th>Ref. 2</th>
<th>Ref. 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 kbar  = 986.923 atm, 1 cm$^3$ atm = 2.4218 $10^{-5}$ kcal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

molal volumes in cm$^3$

$Fe(bcc) \rightleftharpoons Fe(hcp)$

$T^* = 298$ K

$P_{a}^{\circ} = 112\pm8$ kbar = $110,500\pm7900$ atm

$V_{bcc}^{b} = 7.088 - 4.3612 \times 10^{-6}P + 8.0209 \times 10^{-12}P^2 - 5.4181 \times 10^{-18}P^3$

$V_{hcp}^{b} = 6.716 - 4.8869 \times 10^{-6}P + 2.6245 \times 10^{-11}P^2 - 9.942 \times 10^{-17}P^3$

$1 - 110,500$ atm

(A) 1.01

$\frac{dP_c}{dT} = -.033$ kbar deg$^{-1} = -32.6$ atm deg$^{-1}$

(B) 18.41

$\Delta V^d = -.34$ cm$^3$/g.a.

(C)

+0.09

$\Delta H_{298} = +.080$ kcal/g.a.

(E)

(D) 0.08

(F) -17.45

(G) -1.07

$\Delta H_0^\circ = +1.07\pm.13$ kcal mole$^{-1}$
TABLE II

Evaluation of $\Delta H^\circ$ for Cs

$^a$Ref. 2. $^b$Ref. 18. $^c$Ref. 17.

Cs I (bcc) $\equiv$ Cs II (fcc)

<table>
<thead>
<tr>
<th>$T^\ast$</th>
<th>$P^\ast$</th>
<th>$\Delta V^b$</th>
<th>$\Delta H^b_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>23.7 kbar</td>
<td>-.42 cm$^3$/g.a.</td>
<td>-.060 kcal/g.a.</td>
</tr>
</tbody>
</table>

$V^b_{\text{bcc}} = 70.1 - 3.7114 \times 10^{-3}P + 2.8310 \times 10^{-7}P^2 - 1.0944 \times 10^{-11}P^3$

$V^b_{\text{fcc}} = 68.4 + 8.3623 \times 10^{-7}P - 8.2065 \times 10^{-7}P^2 + 6.3507 \times 10^{-11}P^3$

1 - 10,000 atm

$V^b_{\text{bcc}} = 43.965 + 2.2389 \times 10^{-3}P - 2.0373 \times 10^{-7}P^2 + 4.3742 \times 10^{-12}P^3$

$V^b_{\text{fcc}} = 49.52 + 1.0805 \times 10^{-3}P - 1.4354 \times 10^{-7}P^2 + 3.4509 \times 10^{-12}P^3$

10,000 - 23390 atm

$\frac{dP}{dT} = .02$ kbar/deg = 19.7 atm/deg

$\Delta H^b = +.66 \pm .05$ kcal mole$^{-1}$
TABLE III

Evaluation of $\Delta H^\circ$ for Ba

$^a$Ref. 2. $^b$Ref. 5. $^c$Ref. 21. $^d$Ref. 23. $^e$Ref. 20.

Ba I (bcc) $\rightleftharpoons$ Ba II (hcp)

$T^* = 298 \text{ K}$

$P^* = 55.3 \text{ kbar} = 54577 \text{ atm}^a$

$V_{\text{bcc}}^{b,c,d} = 38.26 - 4.0977 \times 10^{-4} P + 5.9825 \times 10^{-9} P^2 - 4.9465 \times 10^{-14} P^3$

$V_{\text{hcp}} = 37.34 - 4.0683 \times 10^{-4} P + 6.0914 \times 10^{-9} P^2 - 5.1304 \times 10^{-14} P^3$

(A) 1.54

$\frac{dP^e}{dT} = .018 \text{ kbar/deg} = 17.8 \text{ atm/deg}$

(B) 40.98

$\Delta V^e = -.72 \text{ cm}^3$

(C) +.08

$\Delta H_{298} = -.091 \text{ kcal/g.a.}$

(D) -.09

(E)

(F) -39.92

(G) -1.54

$\Delta H^\circ = +1.05 \pm .7 \text{ kcal mole}^{-1}$
TABLE IV

Evaluation of $\Delta H^\circ_0$ for Hg

$^a$Ref. 4. $^b$Ref. 22.

Hg (rhombohedral) $\rightleftharpoons$ Hg (bct)

$T^* = 152$ K

$P^* = 6.41$ kbar, $= 6330$ atm$^a$

$v^a_{rh} = 13.976 - 4.5414 \times 10^{-5} P = 7.6389 \times 10^{-11} p^2 + 6.5278 \times 10^{-14} p^2$

$v^a_{bct} = 13.757 - 2.6322 \times 10^{-5} P - 1.9444 \times 10^{-9} p^2 + 1.7778 \times 10^{-13} p^2$

$1 - 6330$ atm

(A) .76

\[
\frac{dP}{dT} = \frac{4744.3}{T} + 13.649 + .87374(T-79) \text{ atm/deg}^b
\]

(B) 2.12

\[
\frac{dP}{dT} = 109 \text{ atm/deg at 152 K}
\]

(C) -.04

$\Delta V = -.145 \text{ cm}^3/\text{g.a.}^a$

(D) -.06

$\Delta H_{152} = -.058 \text{ kcal/g.a.}$

(E) .04

(F) -2.09

(G) -.76

$\Delta H^\circ_0 = -.03 \pm .02 \text{ kcal mole}^{-1}$
TABLE V

Calculation of Debye temperatures from the equation \( \theta_A = \theta_B (V_B/V_A)^{1/3} (M_B/M_A)^{1/2} \)

\[ a \text{Ref. 14. } b \text{Ref. 5.} \]

\( ^c \text{Calculated using the third law method described in the text.} \)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal</th>
<th>( \theta^a )</th>
<th>( M^a )</th>
<th>( M^b )</th>
<th>( V^b )</th>
<th>( V^b )</th>
<th>( \theta^a )</th>
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</thead>
<tbody>
<tr>
<td>Cs</td>
<td>Na</td>
<td>158</td>
<td>22.99</td>
<td>132.9</td>
<td>23.78</td>
<td>70.93</td>
<td>46</td>
</tr>
<tr>
<td>Cs</td>
<td>K</td>
<td>91</td>
<td>39.10</td>
<td>132.9</td>
<td>45.36</td>
<td>70.93</td>
<td>43</td>
</tr>
<tr>
<td>Ba</td>
<td>Ca</td>
<td>230</td>
<td>40.08</td>
<td>137.3</td>
<td>26.27</td>
<td>38.26</td>
<td>110</td>
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<tr>
<td>Ba</td>
<td>Sr</td>
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<td>87.6</td>
<td>137.3</td>
<td>33.93</td>
<td>38.26</td>
<td>113</td>
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<tr>
<td>Au</td>
<td>Cu</td>
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<td>63.54</td>
<td>197.0</td>
<td>7.11</td>
<td>10.21</td>
<td>173</td>
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<tr>
<td>( \alpha )-Sn</td>
<td>( \beta )-Sn</td>
<td>199</td>
<td>118.7</td>
<td>118.7</td>
<td>20.57</td>
<td>16.29</td>
<td>215</td>
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<tr>
<td>hcp Ba</td>
<td>bcc Ba</td>
<td>110</td>
<td>137.3</td>
<td>137.3</td>
<td>38.26</td>
<td>37.34</td>
<td>110.9</td>
</tr>
<tr>
<td>bct Hg</td>
<td>rhomb Hg</td>
<td>71.9</td>
<td>200.6</td>
<td>200.6</td>
<td>13.976</td>
<td>13.757</td>
<td>72.28</td>
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<tr>
<td>fcc Cs</td>
<td>bcc Cs</td>
<td>38</td>
<td>132.9</td>
<td>132.9</td>
<td>70.1</td>
<td>68.4</td>
<td>38.31</td>
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References


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