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Raymond L. Orr and John Chipman

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Thermodynamic Functions of Iron

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Abstract

Recently reported high-temperature thermal data have been incorporated in a review of the thermodynamic properties of iron. The recent data permit more consistent and reliable choices to be made for many of the properties, resulting in better established tabulations of the thermodynamic functions. Values of Cp, $H^\circ_T - H^\circ_{298}$, $S^\circ_T - S^\circ_{298}$, and $(G^\circ_T - H^\circ_{298})/T$ are tabulated for the solid and liquid phases of iron in both stable and metastable regions. Consistency of the tabulations has been maintained to the precision necessary to yield the Gibbs energy change between the bcc (α, δ) and fcc (γ) phases of iron at temperatures pertinent to alloy studies.

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The importance of the metal iron has stimulated many investigations of its thermodynamic properties at elevated temperatures. Reviews and summaries of the data have appeared from time to time. Among these the 1951 paper of Darken and Smith[1] deserves highest recognition for the quality of its criticism and for the precision and thermodynamic consistency of its tabulations. These and the more recent table of Kaufman, Clougherty and Weiss[2] reproduce the Gibbs energy of the $(\alpha, \delta) - \gamma$ transformation with sufficient sensitivity for alloy studies. Other recent compilations of equal validity[3,4,5,6] make no attempt to do this. Since this Gibbs energy change is not greater than 22 cal per g-atom over the temperature range 1100-1800°K it is obviously desirable to tabulate values of $(G^\circ_T - H^\circ_{298})/T$ to four places of decimals even though the absolute accuracy would not warrant such precision. The necessity for reconsideration of the problem is emphasized by the recent publication of several important researches on the enthalpy and heat capacity of iron. The older work is well covered in the reviews cited and will be mentioned here only when actually employed in the tabulations.

GAMMA IRON

Transition temperatures are taken from the selections of Elliott and Gleiser,[5] based on the work of Boulanger[7] and earlier workers. For the $\alpha - \gamma$ (A3) transition at 1184°K we retain the value 215 cal/g-atom adopted by Darken and Smith.[1] It has received confirmation in the recent work of Dench and Kubaschewski,[8] and of Braun[9] using adiabatic calorimetry, and of Wallace, Sidles and Davidson[10] using a pulse heating technic. The enthalpy data of Olette and Ferrier[11] and of Anderson and Hultgren[12] at higher and lower temperatures may be extended to 1184°K to give the following values which are adjusted to the required value of ΔH_{1184}:

$$H^\circ_{\alpha,1184} - H^\circ_{\alpha,298} = 8030 \text{ cal/g-atom} \quad (1)$$

$$H^\circ_{\gamma,1184} - H^\circ_{\alpha,298} = 8245 \text{ cal/g-atom} \quad (2)$$

Olette and Ferrier[11] proposed a constant heat capacity of γ. Their enthalpy data, however, fit an obviously curved line and, moreover, all other workers have found that Cp_γ increases with temperature. The mean value $\overline{Cp}_\gamma = (H^\circ_T - H^\circ_{1184})/(T - 1184)$ is plotted in Fig. 1 for their data and for those of Anderson and Hultgren.[12] If we adopt $Cp_\gamma = 8.1$ cal/deg g-atom at 1184°K, a mean among the three recent adiabatic values,[8, 9, 10] the resulting straight line corresponds to:

$$Cp_\gamma = 5.73 + 0.0020\ T \text{ cal/deg g-atom} \quad (3)$$

In the lower part of Fig. 1 this is compared with the recent direct observations with which it is seen to be in good agreement. The enthalpy increment of γ between 1184°K (A3) and 1665°K (A4) is by this equation, 4127 cal/g-atom, which yields:

$$H^\circ_{\gamma,1665} - H^\circ_{\alpha,298} = 12372 \text{ cal/g-atom} \quad (4)$$

DELTA IRON

Experimental and tabulated values of $\Delta H_{\gamma-\delta}$ have ranged from 100 to 260 cal/g-atom. Darken and Smith[1] calculated 189 cal/g-atom from the iron-carbon diagram but used 165 cal/g-atom in their tabulation. Hultgren et al.[6] accepted 260±50 cal/g-atom. Most recently, Dench and Kubaschewski[8] found 200 cal/g-atom and Braun[9] found 203 cal/g-atom, both by direct measurement.

Recent enthalpy data for δ are consistent with the latter two values. From measurements over the full δ-region, Ferrier and Olette[13] reported

$H^\circ_{\delta,T} - H^\circ_{\alpha,298} = 9.998\ T - 4083$. At the $\gamma - \delta$ (A4) transition temperature, 1665°K, this gives $H^\circ_{\delta,1665} - H^\circ_{\alpha,298} = 12564$ cal/g-atom, and along with Eq. (4), the value $\Delta H_{\gamma-\delta} = 192$ cal/g-atom. This is substantially lower than the value, 263±70 cal/g-atom, deduced by Ferrier and Olette, the difference being altogether in the equation for the heat capacity of γ, which is better represented by our Eq. (3) than by that of Olette and Ferrier.[11] From enthalpy measurements on δ over a smaller range of temperature (1725°- 1807°K), Morris, Foerster, Schultz, and Zellars[14] reported $H^\circ_{\delta,T} - H^\circ_{\alpha,298} = 10.109\,T - 4262$. When extrapolated to 1665°K, this yields $H^\circ_{\delta,1665} - H^\circ_{\alpha,298} = 12569$ cal/g-atom and, along with Eq. (4), $\Delta H_{\gamma-\delta} =$ 197 cal/g-atom.

The value of Cp_δ found by Dench and Kubaschewski,[8] 9.96 at 1673°K, agrees well with the enthalpy data; while those of Braun,[9] 9.51 at 1665°K to 9.87 at 1800°K, are slightly lower. We adopt the values $\Delta H_{\gamma-\delta} = 200$ cal/g-atom and an average Cp for δ of 10.00 cal/deg g-atom to give:

$$H^\circ_{\delta,1665} - H^\circ_{\alpha,298} = 12572 \text{ cal/g-atom} \qquad (5)$$

and

$$H^\circ_{\delta,1809} - H^\circ_{\alpha,298} = 14012 \text{ cal/g-atom} \qquad (6)$$

ALPHA IRON

From 298°K to the ferromagnetic Curie temperature, taken here as 1042°K,[5,7] the recent Cp measurements of Braun[9] and of Wallace et al.[10] are in good agreement. For the most part their data are in substantially good agreement with the best earlier Cp data in that region, except in the 200° range below T_c, where the older values tend to be somewhat higher. Above 1042°K, however, the recent data,[8,9,10] which in this range include those of Dench and Kubaschewski,[8] scatter widely, as also do the older values.

The adopted curve for Cp_{α}, shown in Fig. 2, was drawn such that integration would yield values of $H^{\circ}_{\alpha,T} - H^{\circ}_{\alpha,298}$ which agreed with the enthalpy measurements of Anderson and Hultgren,[12] well within experimental uncertainty, and with the requirement of Eq. (1) at 1184°K. Agreement with the older but quite extensive enthalpy data of Jaeger, Rosenbohm, and Zuithoff[15] was also found to be excellent. The adopted Cp curve joins smoothly with that of Kelley[16] for T < 298°K. Below T_c, it follows the recent Cp data very closely except in the range between 700° and 900°K where the curve was raised slightly in order to agree better with the enthalpy data. Even here the maximum deviation from the measured values is less than 2 pct. Above T_c, agreement is best with the Cp data of Dench and Kubaschewski;[8] the deviation of their values from the adopted curve corresponds closely to that in the γ-phase.

METASTABLE BCC IRON

Between 1184° and 1809°K a smooth curve for the heat capacity of bcc-iron was drawn which was in agreement with the values already adopted and which satisfied the requirement that $\Delta G_{(\alpha,\delta)-\gamma} = 0$ at 1184° and 1665°K. Above 1450°K the curve is linear and is given by:

$$Cp_{\alpha,\delta} = 5.830 + 0.0024\ T \quad (1450°\text{-}1809°K) \qquad (7)$$

Within the stable δ-region, 1665°-1809°K, the average value of Cp_{δ} from Eq. (7) is 10.00 cal/deg g-atom, in good agreement with the experimental data for δ discussed previously. The adopted curves are shown in Fig. 2.

LIQUID IRON

The heat of fusion of δ at 1809°K was measured by Ferrier and Olette,[13] who reported 3292 ± 80 cal/g-atom. Ferrier[17] also reported calculations from the phase diagrams, Fe-P, Fe-S, and Fe-C, all based on modern data. In the last two systems activity data in the solid and liquid phases are available and the accuracy of the calculations is very good. As an average of these studies, they[13] suggest $\Delta H_{1809} = 3300 \pm 100$ cal/g-atom. This value is in complete agreement with the recent determinations of Morris et al.[14] who reported $\Delta H_{1808} = 3298 \pm 100$ cal/g-atom. This agreement effectively disposes of any argument that might be advanced in favor of the older, higher values. The value, $\Delta H_{\delta-\ell, 1809} = 3300$ cal/g-atom, is adopted, which, with Eq. (6), yields:

$$H^\circ_{\ell, 1809} - H^\circ_{\alpha, 298} = 17312 \text{ cal/g-atom} \qquad (8)$$

Enthalpy data for the liquid measured by Ferrier and Olette[13] in the range 1809°- 2210°K gave a heat capacity of 11.226 cal/deg g-atom. The enthalpy data of Morris et al.[14] covered a much shorter range of temperature (1808°- 1875°K); the average Cp was 9.766 cal/deg g-atom. The enthalpy data are in better agreement than would appear from these average heat capacities and both sets of data are adequately represented by the adopted value:

$$Cp_{\ell} = 11.00 \text{ cal/deg g-atom} \qquad (9)$$

The hypothetical metastable melting point of γ is of interest in phase diagram construction. This temperature may be calculated from the adopted functions, which yield $\Delta G_{\gamma-\ell} = 0$ at 1798°K and $\Delta H_{\gamma-\ell, 1798} = 3597$ cal/g-atom.

THE TABULATIONS

The thermodynamic functions for the solid and liquid phases of iron, calculated from the foregoing considerations are given in Tables I and II. The value $S^\circ_{\alpha, 298}$ = 6.52 cal/deg g-atom was taken from Hultgren et al.[6] As mentioned previously, the calculations have been carried out to a precision greater than that warranted by the absolute accuracy of the values, in order to maintain an internal consistency equivalent to 1 cal/g-atom in the Gibbs energy changes for the $(\alpha, \delta) - \gamma$ transformation. Enthalpy increment values, initially carried to 0.1 cal/g-atom, have been rounded off to the nearest calorie in the tables. Values beyond the stable ranges for $Fe_{(\gamma)}$ and $Fe_{(\ell)}$ and for $Fe_{(\delta)}$ above 1809°K result from extrapolations of the adopted Cp equations. The adopted equilibrium transformation functions are summarized in Table III. Finally, Table IV lists values for the Gibbs energy change for $Fe_{(\alpha, \delta)} \rightarrow Fe_{(\ell)}$ over the pertinent temperature range.

ACKNOWLEDGMENTS

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Table I. Thermodynamic Functions for Solid Iron[a]

	$Fe_{(\alpha,\delta)}$				$Fe_{(\gamma)}$			
T, °K	Cp cal/deg g-atom	$H^\circ_T - H^\circ_{298}$ cal/g-atom	$S^\circ_T - S^\circ_{298}$ cal/deg g-atom	$\frac{-(G^\circ_T - H^\circ_{298})}{T}$ cal/deg g-atom	Cp cal/deg g-atom	$H^\circ_T - H^\circ_{\alpha,298}$ cal/g-atom	$S^\circ_T - S^\circ_{\alpha,298}$ cal/deg g-atom	$\frac{-(G^\circ_T - H^\circ_{\alpha,298})}{T}$ cal/deg g-atom
298.15	5.97	0	0.0000	6.5200				
300	5.98	11	0.0369	6.5202				
400	6.54	637	1.8340	6.7615				
500	7.10	1319	3.3535	7.2355	*6.73*	*3174*	*5.3238*	*5.4958*
600	7.66	2057	4.6975	7.7892	*6.93*	*3857*	*6.5685*	*6.6602*
700	8.27	2852	5.9222	8.3675	*7.13*	*4560*	*7.6518*	*7.6575*
800	9.07	3717	7.0754	8.9494	*7.33*	*5283*	*8.6169*	*8.5332*
850	9.61	4183	7.6408	9.2394	*7.43*	*5652*	*9.0643*	*8.9349*
900	10.30	4680	8.2088	9.5285	*7.53*	*6026*	*9.4918*	*9.3162*
950	11.29	5218	8.7905	9.8174	*7.63*	*6405*	*9.9016*	*9.6795*
1000	13.01	5820	9.4073	10.1073	*7.73*	*6789*	*10.2955*	*10.0265*
1020	14.34	6092	9.6769	10.2241	*7.77*	*6944*	*10.4490*	*10.1612*
1030	15.55	6241	9.8220	10.2827	*7.79*	*7022*	*10.5249*	*10.2276*
1042 (T_c)	20.00	6448	10.0216	10.3535	*7.81*	*7115*	*10.6153*	*10.3067*
1050	13.03	6563	10.1318	10.4011	*7.83*	*7178*	*10.6751*	*10.3589*
1060	12.31	6690	10.2515	10.4607	*7.85*	*7256*	*10.7495*	*10.4238*
1080	11.58	6928	10.4742	10.5796	*7.89*	*7414*	*10.8965*	*10.5519*
1100	11.09	7154	10.6820	10.6982	*7.93*	*7572*	*11.0416*	*10.6780*
1184 ($T_{\alpha-\gamma}$)	9.90	8030	11.4497	11.1876	8.10	8245	11.6313	11.1876
1200	*9.75*	*8187*	*11.5816*	*11.2790*	8.13	8375	11.7402	11.2810
1300	*9.26*	*9132*	*12.3382*	*11.8335*	8.33	9198	12.3988	11.8434
1400	*9.21*	*10052*	*13.0199*	*12.3599*	8.53	10041	13.0235	12.3714
1500	*9.43*	*10983*	*13.6625*	*12.8602*	8.73	10904	13.6188	12.8695
1600	*9.67*	*11938*	*14.2787*	*13.3372*	8.93	11787	14.1886	13.3417
1665 ($T_{\gamma-\delta}$)	9.83	12572	14.6669	13.6363	9.06	12372	14.5468	13.6363
1700	9.91	12917	14.8722	13.7937	*9.13*	*12690*	*14.7360*	*13.7913*
1800	10.15	13920	15.4454	14.2318	*9.33*	*13613*	*15.2635*	*14.2207*
1809 (T_m)	10.17	14012	15.4961	14.2704	*9.35*	*13697*	*15.3101*	*14.2585*
1900	*10.39*	*14947*	*16.0006*	*14.6536*	*9.53*	*14556*	*15.7733*	*14.6323*
2000	*10.63*	*15998*	*16.5397*	*15.0655*	*9.73*	*15519*	*16.2673*	*15.0278*

[a] H°_{298} and S°_{298} refer to $Fe_{(\alpha)}$ in all cases. Functions for metastable phases are given in italics. From Hultgren et al.[6]: $H^\circ_{\alpha,298} - H^\circ_{\alpha,0}$ = 1073 cal/g-atom and $S^\circ_{\alpha,298}$ = 6.52 cal/deg g-atom.

Table II. Thermodynamic Functions for Liquid Iron[a]

T, °K	Cp cal/deg g-atom	$H^\circ_T - H^\circ_{\alpha, 298}$ cal/g-atom	$S^\circ_T - S^\circ_{\alpha, 298}$ cal/deg g-atom	$\frac{-(G^\circ_T - H^\circ_{\alpha, 298})}{T}$ cal/deg g-atom
1200	*11.00*	*10613*	*12.8053*	*10.4811*
1300	*11.00*	*11713*	*13.6858*	*11.1958*
1400	*11.00*	*12813*	*14.5010*	*11.8689*
1500	*11.00*	*13913*	*15.2599*	*12.5046*
1600	*11.00*	*15013*	*15.9698*	*13.1067*
1700	*11.00*	*16113*	*16.6367*	*13.6785*
1800	*11.00*	*17213*	*17.2654*	*14.2226*
1809 (T_m)	11.00	17312	17.3203	14.2704
1900	11.00	18313	17.8602	14.7418
2000	11.00	19413	18.4244	15.2379
2100	11.00	20513	18.9611	15.7130
2200	11.00	21613	19.4728	16.1687
2300	11.00	22713	19.9618	16.6066
2400	11.00	23813	20.4299	17.0278
2500	11.00	24913	20.8790	17.4338
2600	11.00	26013	21.3104	17.8254
2700	11.00	27113	21.7256	18.2037
2800	11.00	28213	22.1256	18.5695
2900	11.00	29313	22.5116	18.9237
3000	11.00	30413	22.8845	19.2668
3100	11.00	31513	23.2452	19.5997
3200	11.00	32613	23.5944	19.9228

[a] H°_{298} and S°_{298} refer to $Fe_{(\alpha)}$. Functions for metastable liquid are given in italics.

Table III. Temperatures, Heats, and Entropies of Transformations in Iron

Transformation	T, °K	ΔH cal/g-atom	ΔS cal/deg g-atom
Ferromagnetic (α)	1042	—	—
$\alpha \rightarrow \gamma$	1184	215	0.1816
$\gamma \rightarrow \delta$	1665	200	0.1201
$\delta \rightarrow \ell$	1809	3300	1.8242

Table IV. Gibbs Energy Change for $Fe_{(\alpha,\delta)} \rightarrow Fe_{(\gamma)}$

T, °K	ΔG/T cal/deg g-atom	ΔG cal/g-atom	T, °K	ΔG/T cal/deg g-atom	ΔG cal/g-atom
500	1.7397	870	1080	0.0277	30
600	1.1290	677	1100	0.0202	22
700	0.7100	497	1184	0.0000	0
800	0.4162	333	1200	-0.0020	- 2
900	0.2123	191	1300	-0.0099	-13
1000	0.0808	81	1400	-0.0115	-16
1020	0.0629	64	1500	-0.0093	-14
1030	0.0551	57	1600	-0.0045	- 7
1042	0.0468	49	1665	0.0000	0
1050	0.0422	44	1700	0.0024	4
1060	0.0369	39	1800	0.0111	20

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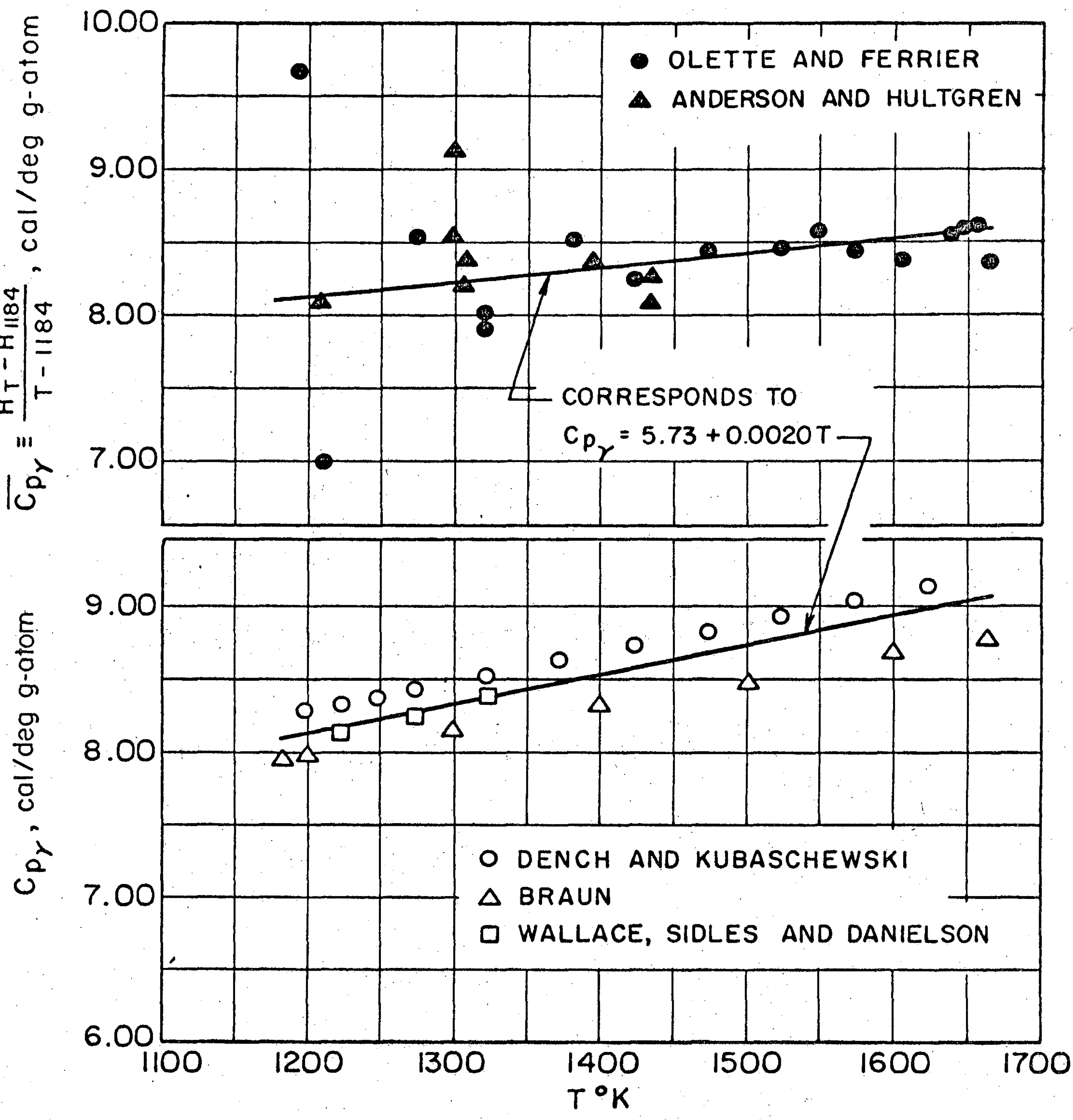

FIG. I HEAT CAPACITY OF GAMMA-IRON.

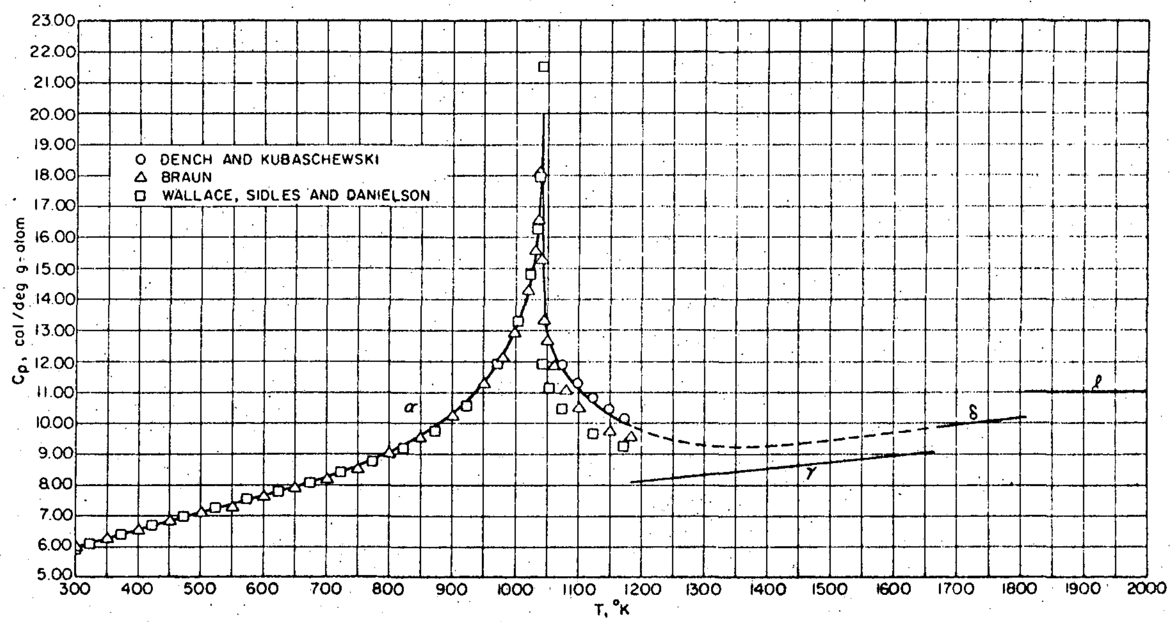

FIG. 2. ADOPTED HEAT CAPACITY CURVES FOR IRON AND RECENT EXPERIMENTAL DATA FOR ALPHA-IRON.

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