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ABSTRACT

Manganese vapor pressures from 1250°- 1500°K were measured by conventional Knudsen and torsion-effusion methods in twelve iron-manganese alloys with compositions from 9-80 at. % Mn. The Knudsen results agreed approximately with previous measurements found in the literature which indicated the solutions were nearly ideal. However, except for the higher Mn compositions, the initial torsion readings indicated much (up to 50%) higher vapor pressures than the Knudsen method. These high readings decreased steadily with time. The results are interpreted as due to depletion of surface concentration of Mn during evaporation. Thus the initial torsion readings are the most nearly correct and Knudsen methods on alloys are to be regarded with suspicion unless it can be demonstrated that diffusion rates are rapid enough to replenish surface concentrations depleted by evaporation. For the lowest Mn contents and highest temperatures, depletion causes initial torsion readings to be too low.

VAPOR PRESSURE STUDIES OF IRON-MANGANESE ALLOYS

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Few thermodynamic data are available for alloys of the high-melting transition metals due primarily to experimental difficulties at the high temperatures involved. Measurement of vapor pressure is one of the most promising techniques to be applied to this problem. From the vapor pressure of a component of an alloy phase, its activity or its partial molar Gibbs energy can be directly calculated. From measurements over a sufficient range of temperatures and compositions the partial and integral Gibbs energy, enthalpies, and entropies may be determined through Gibbs-Duhem integration.

For solid phases of variable composition, which commonly are found in alloys, measured vapor pressures are low because of depletion of the surface concentration of the more volatile component as it is selectively vaporized. Diffusion from the interior tends to restore the depleted concentration. The seriousness of the effect depends on the relative rates of diffusion and vaporization. Although depletion has been recognized as a factor[1] direct measurements of its rate are

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lacking and quantitative estimates of its effect on measurements are uncertain.

In the present work the vapor pressures above a series of iron-manganese alloys have been measured by the torsion effusion method. This method permits a measurement of the vapor pressure of manganese as soon as the sample comes to temperature and continuously throughout the run. The rate of decline of the apparent vapor pressure measures the rate of depletion and the torsion reading at zero time should be correct.

At high-manganese concentrations (70 and 80 at. % Mn), the torsion reading remained nearly constant; surface depletion was negligible. There was a slow drop in measured pressure due to bulk loss of manganese from the sample. However, for lower manganese contents, especially at high temperatures, the depletion effect was considerable and the apparent vapor pressure decreased steadily with time.

For these alloys the Knudsen method should give pressures which are too low. The measurement of pressure in the Knudsen method cannot be made until enough manganese has been vaporized to be weighable. The Knudsen result is therefore an integrated average between the initial and final vapor pressures.

To verify this, conventional Knudsen measurements were also made with results in approximate agreement with previously published Knudsen measurements[1,4,5] for these alloys. As expected, for the lower manganese contents the initial torsion readings of pressure were as much as 50% higher than the Knudsen.

The Apparatus

The apparatus, shown in Fig. 1, is capable of operating to temperatures up to 2000°K. A vacuum of 5×10^{-6}mm Hg can be maintained. Temperatures were measured to ±3°K by a tungsten-rhenium thermocouple placed in the dummy cell, N. The torsion cell consisted of two alumina crucibles with holes in their covers. They were placed in the molybdenum holder shown suspended from the torsion wire. Rectangular torsion wires (1×4mm) were found to have superior sensitivity and less residual distortion than circular (2mm diameter) wires. The precision of angular measurement was found to be ±0.025 degrees; the variation is no doubt due to temperature fluctuation and vibration. For the Knudsen experiments the alumina cell was set on the support, N.

Sample Preparation

Eight-hundred gram samples were prepared by melting together electrolytic iron and electrolytic manganese and pouring the melt into a water cooled copper mold. Melting and pouring were done under a helium atmosphere. The metals used were said to be 99.95% pure; no impurities were detected in a spectrographic analysis of the alloys. Segregation in the alloy was demonstrated to be negligible by electron probe analysis; the closeness of liquidus to solidus and the rapid rate of freezing produced a non segregated solid. Samples were chemically analysed by wet methods for iron and manganese content. Samples were used in finely divided form to increase the surface area.

Torsion Effusion Measurements

The apparatus was calibrated over the approximate temperature range 1250°-1500°K by measurements of pure manganese. For each setup

a single calibration constant, expressed in atmospheres per degree of torque, gave results agreeing, usually within ±2%, with the vapor pressure of manganese[2] over the entire temperature range. Thus systematic errors in hole size, temperature measurement, and other constants of the apparatus were included in the calibration constant.

The irregular holes made calibration particularly necessary, otherwise errors in excess of ±15% would have been made. The smaller holes were drilled in the alumina with supersonic drills using diamond abrasive while larger holes were drilled with conventional diamond drills. The resulting holes were irregularly circular. No attempt was made to make knife edges.

Vapor pressures of the alloys were measured with the same crucibles and holes as with pure manganese. Hence the thermodynamically significant measured quantity

$$a_{Mn} = \phi(\text{alloy})/\phi(\text{pure Mn})$$

is simply the ratio of the torque angles (ϕ) for alloy and pure Mn. Systematic errors were therefore nearly eliminated.

After inserting a sample, the crucibles were heated to 700-800 °K for some hours to bake out possible volatile components. Usually no deflection was observed during this stage. The sample was then heated rapidly to the temperature of measurement. As it reached this temperature, maximum torque was developed, which then decreased slowly or rapidly. As would be expected, the surface depletion effect increased with lower manganese contents, higher temperatures, and larger hole sizes. In the 9 atomic percent manganese alloy at the highest temperature, detectable depletion occurred in a time sufficient to volatilize only about 1 microgram of manganese from a 10 gram sample.

From the initial torsion readings activities and Gibbs energies were calculated. In the form of $\Delta\bar{G}_{Mn}^{xs}$ the experimental results are shown in Fig. 2. The points plotted as circles were read in the following sequence. After preheating, the sample was raised within 2-3 minutes to the lowest temperature of the run and the deflection read. The temperature was then increased and the deflection read after it remained constant for about thirty seconds, and so on to the highest temperature. The time between temperatures became increasingly shorter as the temperature was raised. "SHORT RUNS" represent readings of fresh samples brought directly to the temperature of test. "COOLING RUNS" represent readings taken during cooling after readings were taken up to the maximum temperature.

Except at the highest temperatures, the values cluster satisfactorily about the straight lines on the graph. The slopes of the lines

$$d\Delta\bar{G}_{Mn}^{xs}/dT = -\Delta\bar{S}_{Mn}^{xs}$$

yield the partial molar entropies. High-temperature deviations are always in the direction of low pressures and occur only in those runs were the surface depletion effect is large. Except for these runs it must be concluded that the initial torsion readings give self-consistent results.

From these data, with the aid of Gibbs-Duhem integration, the partial and integral quantities given in Tables 1 and 2 were calculated. The integral values are shown in Figure 3 along with values of ΔH determined by acid solution calorimetry[3]. Agreement of the ΔH values obtained by this entirely different method is a valuable confirmation of the accuracy of the vapor pressure results.

Knudsen Measurements

The cells were made of alumina as described for the torsion method. Cells containing samples were maintained at temperature for a sufficient time so that approximately 100 mg of sample had been vaporized after which the cell was weighed to determine the loss in weight. The cell was calibrated as before by the vapor pressure of pure manganese; for which consistent results were obtained. Results at 1450°K for this and previous work are shown along with the torsion results in Fig. 4. Data of the other workers was translated to 1450°K using entropies found in this work.

Discussion

The iron-manganese system shows a positive deviation from Raoult's law for all compositions. The temperature coefficients indicate negative values for $\Delta\bar{S}_{Mn}^{XS}$ at all compositions.

The present data do not agree with the vapor pressure measurements of Butler, McCabe, and Paxton[1], who used a continuous weighing Knudsen cell to determine the activities of manganese in the system. Their data indicated a negative deviation from Raoult's law at all compositions. However, later work from the same laboratory[4], on high concentration manganese alloys only, showed positive deviations from Raoult's law agreeing very well with the present investigation, calculating activities from their previous values[1] for pure manganese. The discrepancies for low manganese alloys were probably due to the surface depletion. Butler, et al.[1] were aware of this phenomenon, and attempted to allow for it by extrapolating their results to zero weight loss.

In the present investigation extrapolations to zero weight loss for the low-Mn high-T measurements were found to be unreliable.

Lyubimov, Granovskaya, and Berenshtein[5] studied the system by collecting the condensed vapors from evaporation from a free surface. The condensate was chemically analysed spectrographically; from the analyses of a series of compositions it might be possible to determine the activities of the components. Although their method is theoretically sound, it can give rise to a considerable uncertainty in this system particularly because of the low fraction of iron in the condensate. Their analyses of the surface concentration of manganese after evaporation showed a depletion of manganese concentration of only two percent. In the present investigation attempts made to evaluate depletion from electron probe analysis failed because of the difficulty of securing level polishing. However, indications were that depletion was severe.

The rate of surface depletion of manganese is a function of the rate of evaporation per unit area and the rate of diffusion. For a standard shape of sample the relation should be readily derivable so that the measurement of any two of the above quantities would permit the calculation of the third. In the present work no attempt to do this was made because the surface area and size and shape of the sample particles were not known. Experiments where these were controlled should be possible, however. Apparent vapor pressures would then give surface concentrations of the volatile component as a function of time, while the rate of evaporation per unit area would also be determinable.

The effect of temperature on the surface depletion should depend on the relative magnitude of the heat of vaporization $\Delta \bar{H}_{V,Mn}$ and the

activation energy of diffusion, Q. For most metals $\Delta\bar{H}_V > Q$ so that the unfavorable effect of depletion should increase with temperature. Values of Q determined by Wells and Mehl[6] were not sufficiently different from $\Delta\bar{H}_{V,Mn}$ to allow the prediction of the pronounced unfavorable effects of temperature found in the present case.

The unfavorable effect of low-Mn concentration is easy to understand. Thus, loss of 2% Mn in a 10% alloy causes a decrease of 20% in the vapor pressure, while in an 80% Mn alloy such a loss would not have a noticeable effect.

At any rate, Knudsen measurements of activities must be regarded with suspicion unless it can be shown that surface depletion is not serious. Torsion methods are applicable except for very severe surface depletion.

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TABLE 1

Partial Molar Quantities for Fe-Mn Alloys at 1450°K

A. Mn Component $Mn_{(\gamma)}$ = Mn (in alloy)$_{(\gamma)}$

x_{Mn}	a_{Mn}	γ_{Mn}	$\Delta \bar{G}_{Mn}$	$\Delta \bar{G}^{xs}_{Mn}$	$\Delta \bar{H}_{Mn}$	$\Delta \bar{S}_{Mn}$	$\Delta \bar{S}^{xs}_{Mn}$
0	0.000	1.524	$-\infty$	1215	-3353	∞	-3.150
0.1	0.143	1.428	-5608	1027	-2966	1.822	-2.754
0.2	0.268	1.341	-3791	846	-2634	0.798	-2.400
0.3	0.388	1.294	-2792	676	-2294	0.344	-2.048
0.4	0.468	1.170	-2121	520	-1954	0.115	-1.706
0.5	0.570	1.141	-1617	381	-1577	0.027	-1.350
	(±0.014)	(±0.027)	(±70)	(±70)	(±400)	(±0.25)	(±0.25)
0.6	0.658	1.097	-1206	265	-1171	0.025	-0.990
0.7	0.742	1.060	-862	166	-755	0.074	-0.635
0.8	0.823	1.029	-561	82	-381	0.124	-0.319
0.9	0.907	1.008	-281	23	-108	0.119	-0.090
1.0	1.000	1.000	0	0	0	0	0

B. Fe Component $Fe_{(\gamma)}$ = Fe (in alloy)$_{(\gamma)}$

x_{Fe}	a_{Fe}	γ_{Fe}	$\Delta \bar{G}_{Fe}$	$\Delta \bar{G}^{xs}_{Fe}$	$\Delta \bar{H}_{Fe}$	$\Delta \bar{S}_{Fe}$	$\Delta \bar{S}^{xs}_{Fe}$
1.0	1.000	1.000	0	0	0	0	0
0.9	0.903	1.003	-294	10	-21	0.188	-0.021
0.8	0.812	1.014	-602	41	-81	0.359	-0.084
0.7	0.724	1.034	-930	98	-196	0.506	-0.203
0.6	0.664	1.066	-1288	183	-380	0.627	-0.388
0.5	0.554	1.108	-1700	296	-667	0.713	-0.664
	(±0.014)	(±0.027)	(±70)	(±70)	(±400)	(±0.25)	(±0.25)
0.4	0.465	1.162	-2208	432	-1201	0.695	-1.126
0.3	0.373	1.242	-2845	623	-1975	0.600	-1.792
0.2	0.271	1.356	-3760	877	-3108	0.450	-2.748
0.1	0.152	1.524	-5420	1215	-4678	0.512	-4.064
0.0	0.000	1.778	$-\infty$	1659	-6779	∞	-5.819

TABLE 2

Integral Quantities for Fe-Mn Alloys at 1450°K

$$(1-x)Fe_{(\gamma)} + xMn_{(\gamma)} = Fe_{(1-x)}Mn_{x(\gamma)}$$
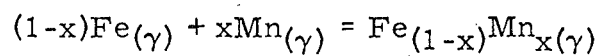
x_{Mn}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0	0	0	0	0	0
0.1	825	- 316	0.351	112	-0.295
0.2	-1240	- 592	0.447	202	-0.548
0.3	-1488	- 825	0.457	272	-0.756
0.4	-1621	-1009	0.422	318	-0.915
0.5	-1659	-1122	0.370	338	-1.007
	(±70)	(±400)	(±0.25)	(±70)	(±0.25)
0.6	-1607	-1183	0.293	332	-1.044
0.7	-1457	-1121	0.232	303	-0.982
0.8	-1200	- 926	0.189	241	-0.805
0.9	- 794	- 564	0.158	142	-0.487
1.0	0	0	0	0	0

LEGEND OF FIGURE 1

A   Stainless steel vacuum chamber

B   Water cooled copper tubes

C   Opening for the suspension mechanism

D   Suspension system

E   Vacuum outlet

F_1 Thermocouple hole

F_2, F_3 Electrical busbar holes

G_1, G_2 Water cooled copper conductors

H_1, H_2 Water cooled copper discs distributing power to heating elements

I   Tungsten heating elements

J   Tripod stand

K   Bottom radiation shields

L   Top radiation shields

M Al_2O_3 tube for thermocouple and Knudsen cell

N   Dummy cell, for the thermocouple
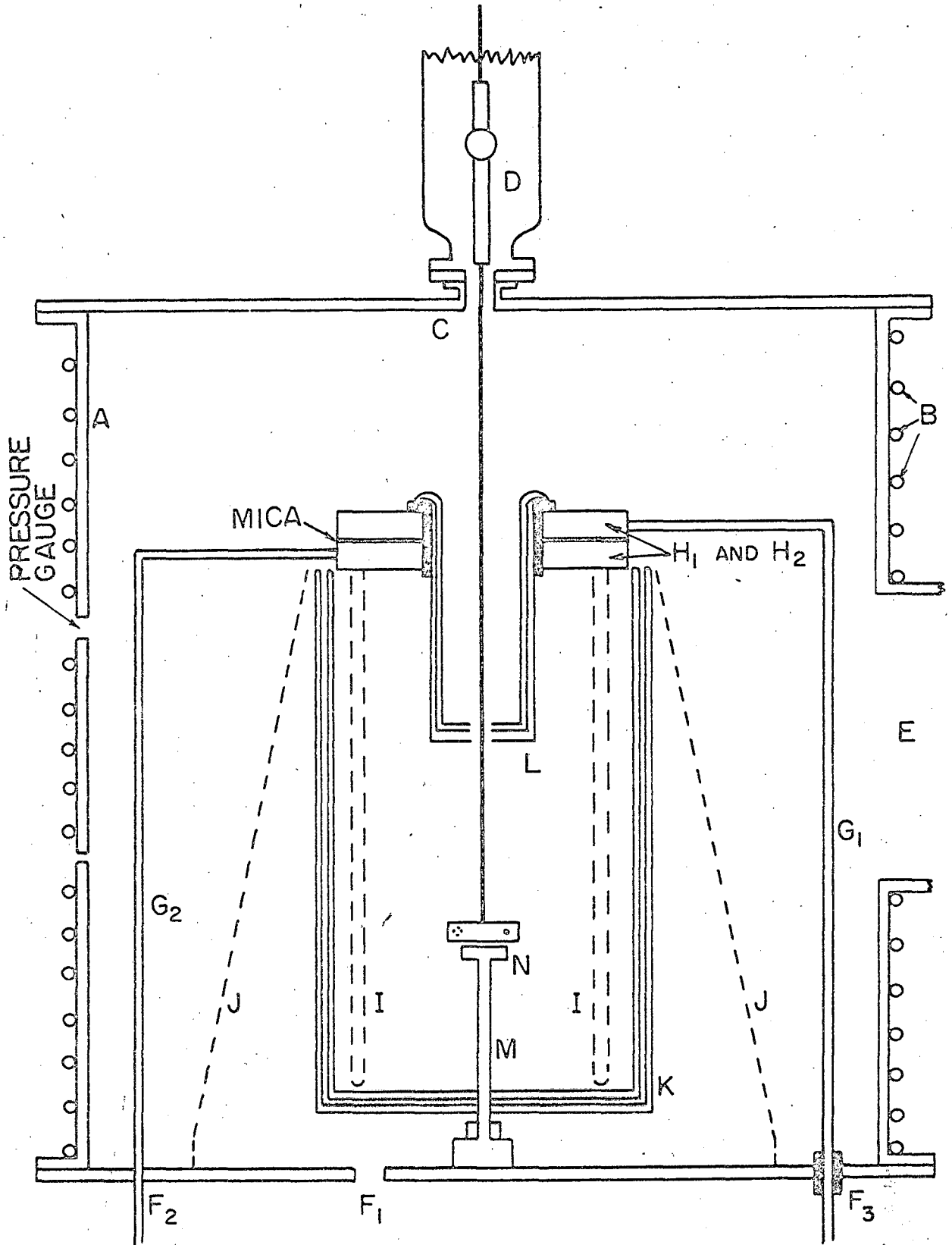
FIG. I   FURNACE ASSEMBLY.
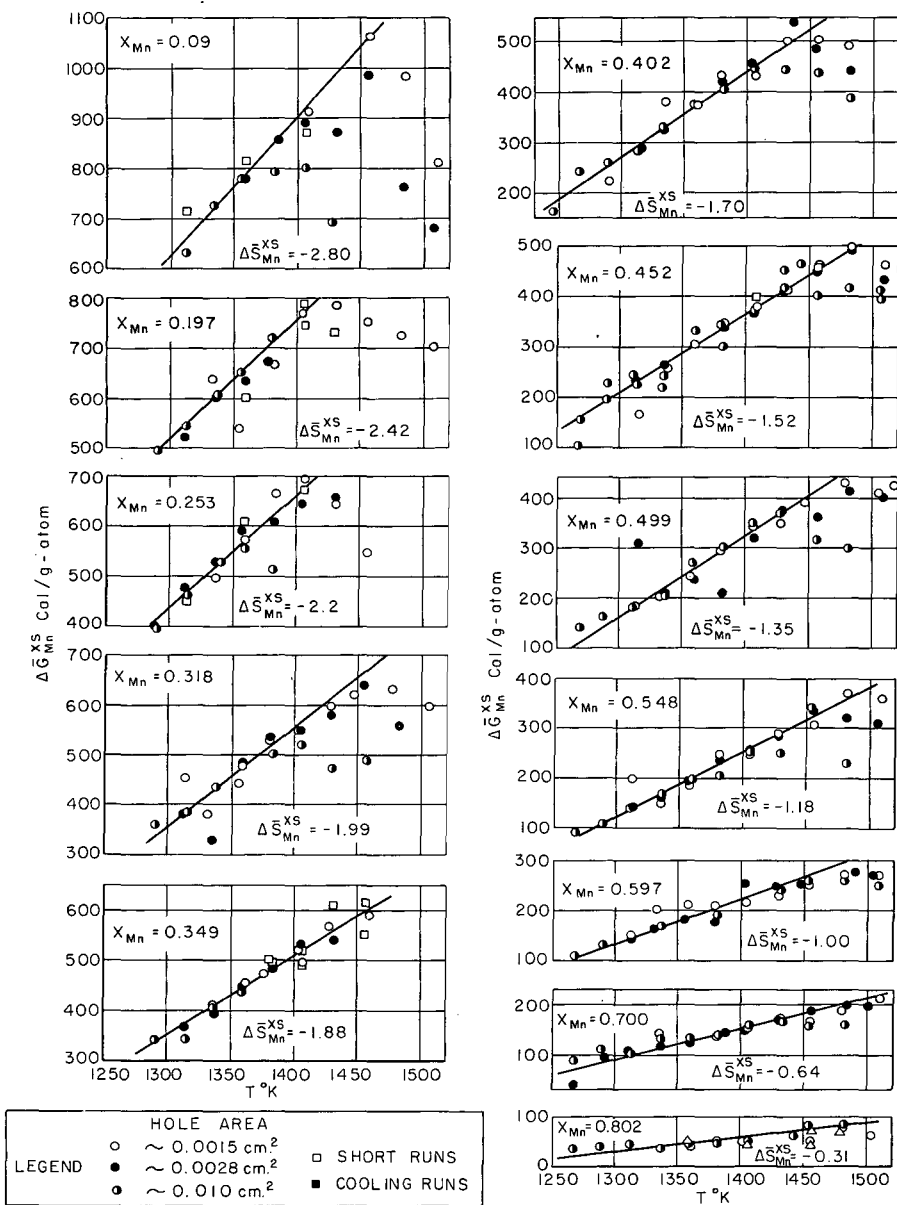
FIG.2 EXPERIMENTAL VALUES OF $\Delta\bar{G}_{Mn}^{XS}$ FOR THE REACTION $Mn_{(\gamma)} \rightarrow Mn_{(ALLOY)}$.

MUB-5036
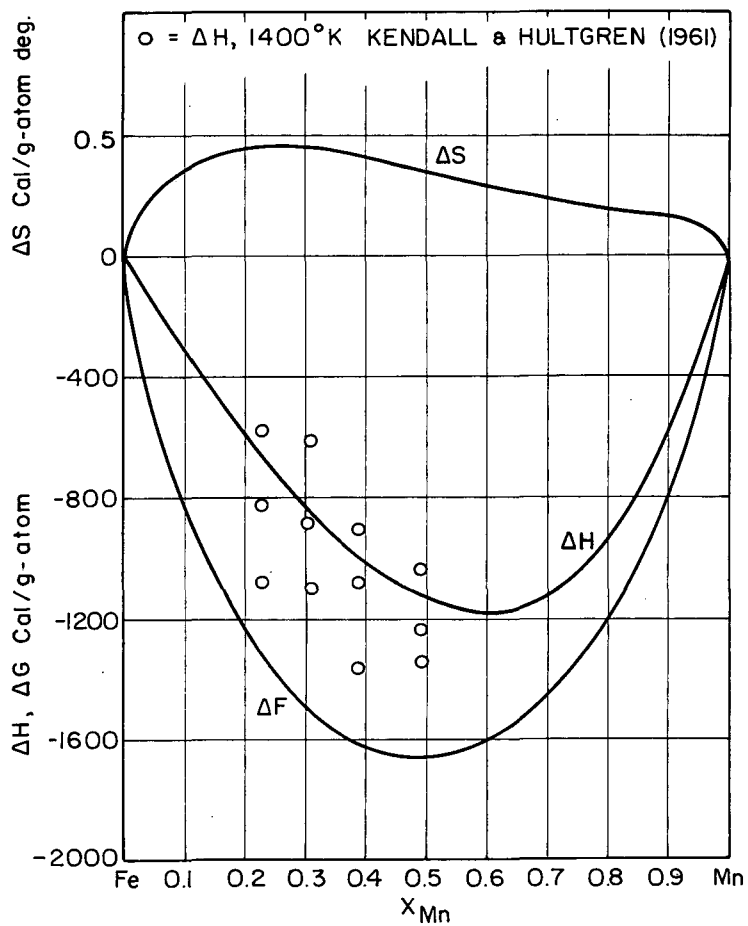
FIG. 3 INTEGRAL QUANTITIES FOR SOLID
IRON-MANGANESE ALLOYS AT 1450°K.

MUB-4069
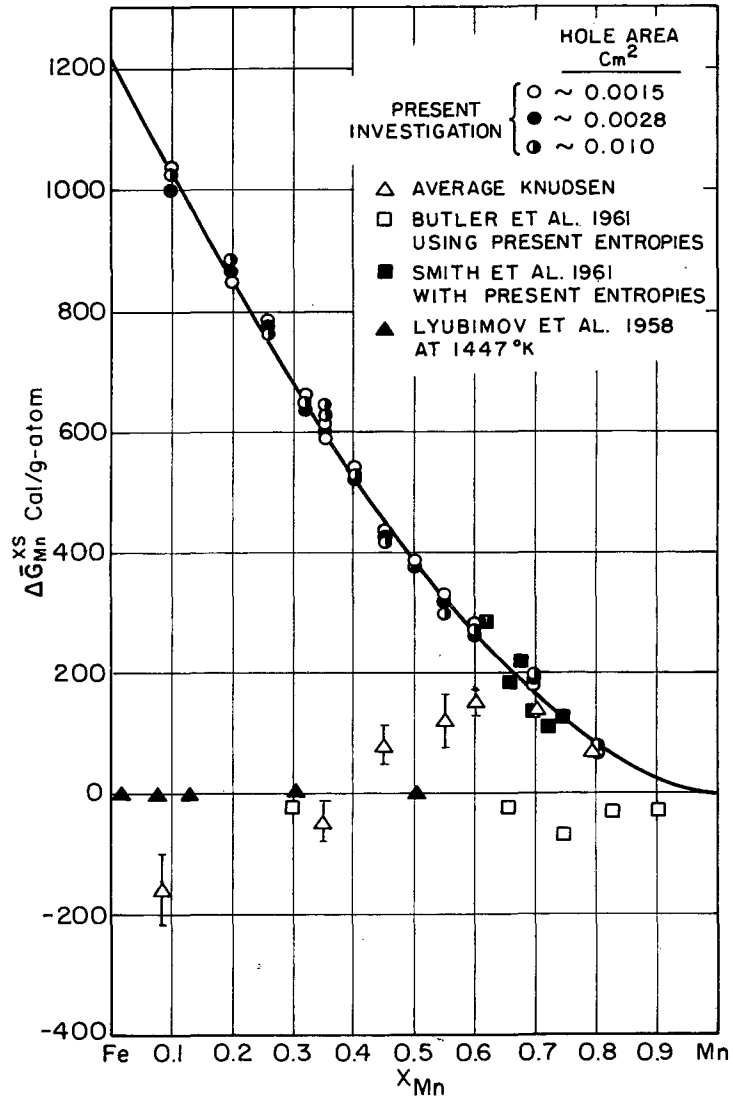
FIG. 4 $\Delta\bar{G}_{Mn}^{XS}$ FOR SOLID IRON-MANGANESE ALLOYS
WITH RESPECT TO γ_{Mn} AT 1450 °K.

MUB-4068