

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

Services Technical Information Agency

limited supply, you are requested to return this copy WHEN IT HAS SERVED its purpose so that it may be made available to other requesters. Your cooperation is appreciated.

38081

GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO LIABILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE AGENCY HAS FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY ANY OTHER PARTY OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PARTY TO REPRODUCE, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, OR TO PATENT, OR OTHERWISE TO INFRINGE ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

CLASSIFIED

AD No. 38 081
ASTIA FILE COPY

CARNEGIE INSTITUTE OF TECHNOLOGY
METALS RESEARCH LABORATORY

RESEARCH REPORT



SULFUR PRESSURE MEASUREMENTS OF IRON SULFIDE

IN EQUILIBRIUM WITH IRON

BY

C. Law McCabe

PITTSBURGH, PENNSYLVANIA, DATE February 2, 1954

Table I. SUMMARY OF EXPERIMENTAL DATA

Cell	a cm ²	Duration of run min.	W.L. grams	T	Run No.
Platinum	0.0248	6855	0.0093	1235	40
"	0.0248	12890	0.0175	1236	42
Silica	0.0287	9967	0.0134	1233	47
"	0.0287	6825	0.0121	1245	54
Armco	0.0329	5760	0.0099	1236	52
"	0.0329	5535	0.0093	1237	53
Zircon	0.0315	9586	0.0146	1235	103
"	"	9550	0.0146	1235	104
"	"	6955	0.0077	1224	105
"	"	6935	0.0118	1245	106
"	"	6720	0.0155	1255	108
"	"	6999	0.0092	1232	109

Table II. CELL DATA

Cell	N_A	f	K
Armco Iron	0.453	0.0196	0.976
Platinum	0.581	0.0100	0.993
Zircon	0.552	0.0121	0.989
Silica	0.526	0.0144	0.987

Table III. CALCULATED S₂ PRESSURE

Run No.	P_{S_2} atm $\times 10^7$	$1/T \times 10^4$
40	0.899	8.097
42	0.900	8.091
52	0.838	8.091
53	0.861	8.084
47	0.771	8.110
54	1.02	8.032
103	0.801	8.097
104	0.795	8.097
105	0.596	8.170
106	0.900	8.032
108	1.21	7.968
109	0.686	8.117

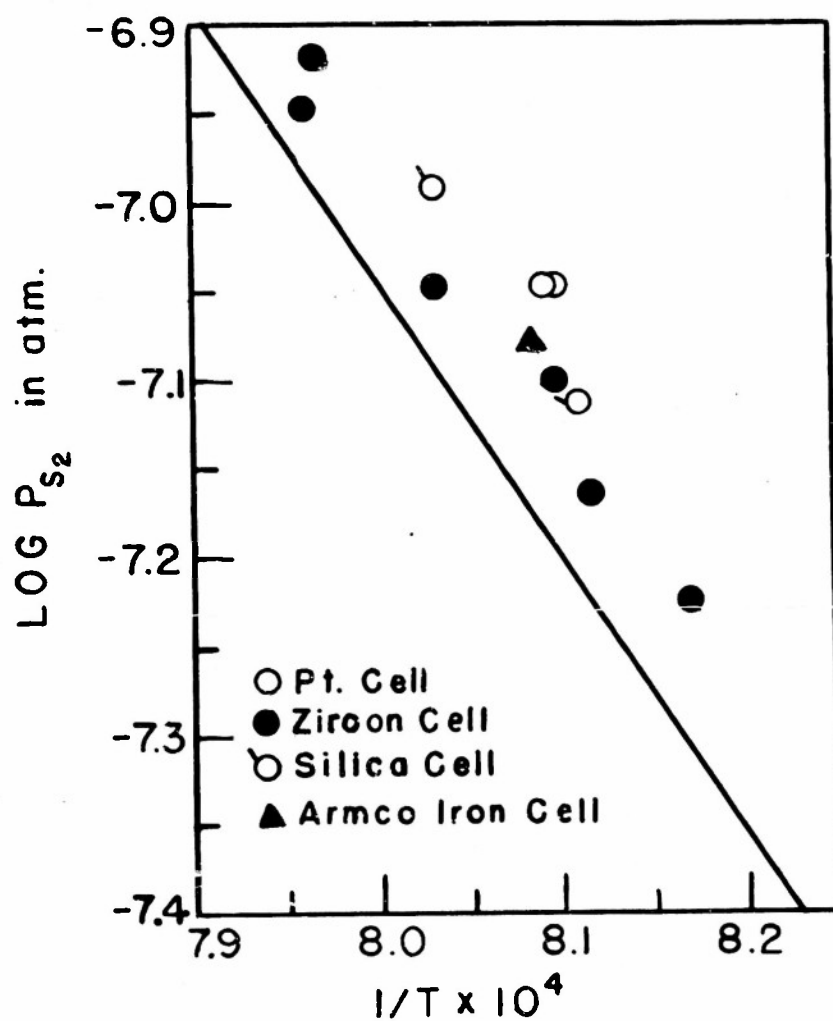


Figure I. Experimental values for $\log P_{S_2}$, calculated from the Knudsen Cell experimentals reported here on the assumption that only S_2 is effusing, vs $1/T$.

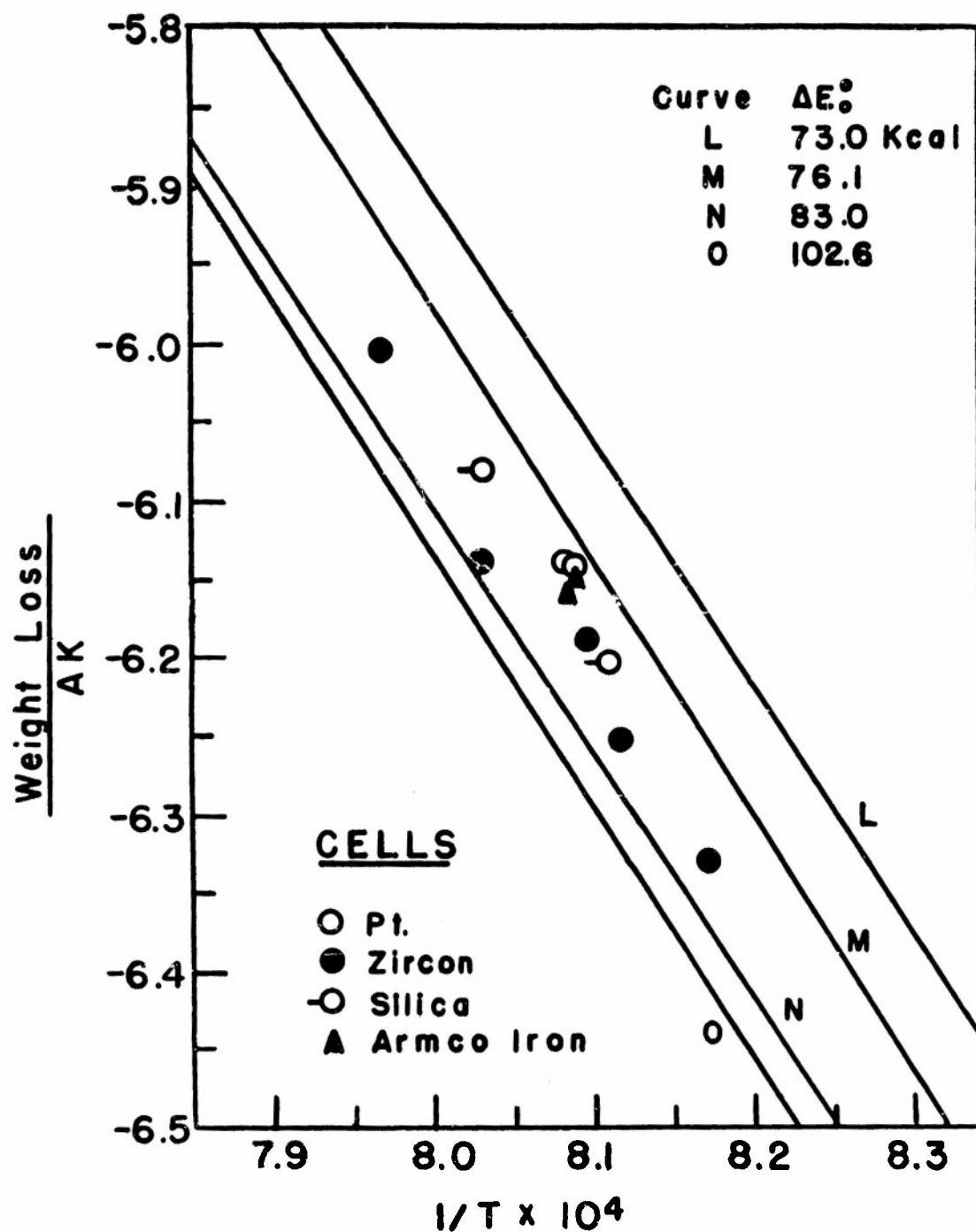


Figure II. Values for $\frac{(W.L.)}{AK}$ vs $1/T$ obtained from the Knudsen Cell experiments reported here and those calculated from the gas equilibria data of Richardson and Alcock in conjunction with the equilibrium constant for the reaction $3S \rightleftharpoons 2S_2$ assuming various suggested values for ΔE for this reaction.

SULFUR PRESSURE MEASUREMENTS OF IRON SULFIDE
IN EQUILIBRIUM WITH IRON

by

C. Law McCabe*

Abstract

Sulfur pressure measurements above iron sulfide in equilibrium with iron have been carried out by the Knudsen Orifice Method. From a comparison of the weight loss of the cell per unit time obtained in the above experiments and that calculated from Richardson and Alcock's measurements of the S_2 pressure above iron sulfide in equilibrium with iron and the dissociation constant for diatomic sulfur from spectroscopic and thermal data, it is concluded that the energy of dissociation of S_2 is not 102.6 kcal. as suggested by Gaydon.

* Junior Member AIME and Assistant Professor, Department of Metallurgy, Carnegie Institute of Technology.

SULFUR PRESSURE MEASUREMENTS OF IRON SULFIDE
IN EQUILIBRIUM WITH IRON

by

C. Law McCabe

Introduction

Extensive equilibrium measurements have been made in the determination of sulfur potentials of a great many systems of metallurgical interest.⁽¹⁾ In order to confirm their reliability, to supply data which could be of use in further thermodynamic calculations, and to establish the reliability of the Knudsen Orifice in obtaining accurate thermodynamic values at high temperatures, the present investigation on the pressure of the gaseous species above iron sulfide in equilibrium with iron has been carried out. The Knudsen Orifice Method has been used for these pressure measurements.

Experimental

The apparatus and general technique for this investigation are the same as that reported for the determination of the vapor pressure of silver in this laboratory.⁽²⁾ To reduce the residual gas pressure in the evacuated chamber, a titanium getter, maintained at run temperature, was introduced. Several types of Knudsen Cells were used-- platinum, Armco iron, zircon, and fused silica. The orifice in the zircon cell was fashioned with a small diamond wheel.

The same precautions were used in this investigation as those which were employed in the work in this laboratory on molybdenum sesquisulfide.⁽³⁾ The weight loss per minute of the Armco cell alone was measured and used to calculate the weight loss of the Fe-FeS mixture when it was in this

cell.

The iron sulfide-iron mixture was prepared by heating a sample of pure FeS_2 , kindly supplied by K. K. Kelley of the Bureau of Mines, with excess iron powder, C. P. grade, obtained from the Fisher Scientific Company. These two substances were heated in a closed Armco iron crucible at 960°C held in a vacuum of less than 10^{-5} mm Hg. for twenty-four hours. The mass was then removed from the cell and ground in an agate mortar. In this form it was charged to the various Knudsen cells. It was found that heating the Knudsen cell for an additional 2 days was sufficient to obtain constant rates of weight loss of the cell. The data obtained in this investigation is recorded in Table I.

To establish whether or not a sulfide of iron is volatile at these temperatures, 0.7646 grams of the iron sulfide-iron mixture, which was described above and contained 69.2% Fe, was placed in the zircon Knudsen cell and runs 103-109 were performed on it. After the completion of these runs, the total amount of iron left in the cell was obtained by chemical analysis. It contained 0.537 grams of Fe, compared to 0.529 grams in the original charge. Thus there was an apparent gain in iron of 1.5%. We attribute this to unknown experimental error and conclude that no sulfide of iron is volatile. The vapor pressure of pure iron⁽⁴⁾ is about one thousandth that of the sulfur pressure⁽¹⁾ at these temperatures. The vapor pressure of iron inside the Knudsen Cell will be almost exactly that of pure iron, since in the iron rich phase the percentage of sulfur is of the order of 0.025%⁽⁵⁾. At this low percentage of sulfur Henry's Law is probably obeyed by the sulfur and thus the iron will obey Raoult's Law. In any event, the vapor pressure of iron will be lower than that

of pure iron and since the vapor pressure of pure iron is negligible compared to the pressure of sulfur, the weight loss of the cell due to the vaporization of iron can be neglected. Thus since neither iron nor iron sulfide is volatile to an appreciable extent, we conclude that the total weight loss of the cell is due to the vaporization of sulfur.

Discussion and Calculations

On the assumption that S_2 is the only gaseous species present in appreciable quantity, its pressure can be calculated from the data in Table I using the ordinary Knudsen formula⁽²⁾. The calculated values are given in Table III and the values are graphed in Figure I. Also, in Figure 1 the pressure of S_2 , calculated from the gas equilibria data of Richardson and Alcock⁽¹⁾, is shown. It is obvious, if one assumes both sets of data are accurate, that some other species is present in the gas phase and is effusing. We feel the data are sufficiently accurate to assume that this discrepancy is due to the presence of monatomic sulfur. Data for the standard free energy of dissociation of diatomic sulfur going to monatomic sulfur have been compiled by Richardson and Jeffes⁽¹⁾. K. K. Kelley⁽⁶⁾ also has done extensive calculations on the standard free energy for this reaction from the spectroscopic energy of dissociation and thermal data. His calculations have been assumed correct and further calculations have been made to obtain the standard free energy of dissociation of S_2 using the other possible spectroscopic values.

A small correction to the pressure calculated by the simple Knudsen formula is necessary to correct for the fact that not all of the molecules vaporizing from the surface of the material whose pressure one is measuring hit the top of the cell. The corrections for this can be found in papers

by C. I. Whitman⁽⁷⁾ and P. Clausing⁽⁸⁾. Table II gives the values needed for this correction. The nomenclature is that of Whitman⁽⁷⁾. $W_B = 1$, since the orifice edge was sharp. No attempt was made to supply the correction for the accommodation coefficient not being equal to one. There is no available data on this quantity for this system and anyway the correction would be small for reasonable values of α .

Using the Knudsen Formula as modified by Whitman⁽⁷⁾ and the assumption that S_2 and S effuse independently and without interaction, the following formula is easily derived.

$$\frac{(W.L.)}{(A)(K)} = K_1^{1/2} P_{S_2}^{1/2} M_S^{1/2} + P_{S_2}^{1/2} M_{S_2}^{1/2} \quad (1)$$

The symbols are identified as follows: K_1 is the dissociation constant for diatomic sulfur going to monatomic sulfur; K has the same definition as that given by Whitman⁽⁷⁾; P is the pressure of the species in question in atmospheres; A is 2658 times the orifice area in square cm. times the duration of the run in minutes divided by T; M is the molecular weight of the particle under consideration; and W.L. is the weight loss of the cell during the run.

The results of the above calculations are shown in Figure 2. Curves L, M, N, and O show $(W.L.)/(K)(A)$ calculated from (1) using the various energies of dissociation of S_2 from spectroscopic data and for curve L from gas density measurements by von Wartenburg and by Nernst⁽¹⁾.

Also, in Figure 2 are tabulated these same values obtained in the experiments reported here. It is seen that these data fall between the values of $(W.L.)/(K)(A)$ from the two lowest values for the spectroscopic energy of dissociation. Taking the experimental points of $(W.L.)/(K)(A)$

for the four cells at $1/T = 8.091 \times 10^{-4}$, the value for the energy of dissociation of S_2 at $0^\circ K$ for the average of the four values is 79 kcal. This is closest to the value $\Delta E_0^\circ = 76$ kcal. Thus, one can conclude that these data favor the lowest spectroscopic value. Although the precision of the Knudsen data reported here is not sufficient to be sure of this conclusion, we can say with reasonable certainty that the value selected by Gaydon⁽⁹⁾ from the spectroscopic data is not the correct one. Further support for this last conclusion is shown by the fact that Richardson and Jeffes⁽¹⁾ selected, $\Delta E_0^\circ = 73$ kcal using von Wartenburg's and Nernst's gas density measurements. Additional experimental work needs to be done using a sulfide with a sulfur potential amenable to Knudsen Orifice measurements at higher temperatures, where the contribution of the monatomic sulfur will be much larger than that due to diatomic sulfur. Then a better estimate of ΔE_0° can be made by comparing these data with thermal or equilibria data.

Acknowledgment

This work was sponsored by the Office of Naval Research. Mr. Robert Miller and Mr. Robert Hudson assisted in the pressure determinations and calculations reported here. The chemical analyses were done by Mrs. Caroline Shaeffer of the Metals Research Laboratory. Mr. C. B. Alcock of the Nuffield Research Group at the Royal School of Mines suggested the problem to the author and has been of great help in the interpretation of the data. The Zircon crucible was donated by the Laboratory Equipment Company, St. Joseph, Michigan. The small, "cemented diamond particle" wheels were donated by the Koebel Diamond Tool Company, Detroit, Michigan.

References

1. F. D. Richardson and J. H. E. Jeffes: Journal of the Iron and Steel Institute, 171, Part 2 (1952), 165.
2. C. E. Birchenall and C. L. McCabe: Jl. of Metals (May 1953), 707.
3. C. L. McCabe: In press.
4. J. W. Edwards, H. L. Johnston, and W. E. Ditmars: Jl. Amer. Chem. Soc. 73 (1951) 4729.
5. J. W. Chipman: Metals Handbook, Amer. Soc. Metals (1948) 1215.
6. K. K. Kelley: Bull. U. S. Bur. Min. (1937) #406.
7. C. I. Whitman: J. Chem. Phys. 20 (1952) 152.
8. P. Clausning: Ann. Physik 12 (1932) 961.
9. A. G. Gaydon: Dissociation Energies, Chapman and Hall Ltd., London (1947).

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

38081

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

**Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO**

UNCLASSIFIED