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HOT COAL GAS DESULFURIZATION
WITH MANGANESE-BASED SORBENTS

Second Technical Report for the Period December 1, 1992 to March 1,
1993

By
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INTRODUCTION

At present, the focus of work being performed on Hot Coal Gas Desulfurization is primarily in the use of zinc ferrite and zinc titanite sorbents; however studies at the U. S. Steel Fundamental Research Laboratories in Monroeville, PA, by E. T. Turkdogan¹ indicate that an alternate sorbent, manganese dioxide-containing ore in mixture with alumina (75 wt% ore + 25 wt% Al₂O₃) may be a preferable alternative to zinc-based sorbents.

A significant domestic source of manganese in Minnesota is being explored for an *in situ* leach process which has potential for producing large tonnages of solutions which may be ideal for precipitation and recovery of pure manganese as a carbonate in a reactive form.

In the current program the following studies will be addressed:

- Preparation of manganese sorbent pellets and characterization tests on pellets for strength and surface area;
- Analysis of the thermodynamics and kinetics of sulfur removal from hot fuel gases by individual sorbent pellets (loading tests) by thermogravimetric testing;
- Regeneration tests via TGA on individual sorbent pellets by oxidation;
- Bench-scale testing on sorbent beds in a two-inch diameter reactor.

The developed information will be of value to METC in its determination of whether or not a manganese-based regenerable sorbent holds real promise for sulfur cleanup of hot fuel gases. This information is necessary prior to pilot-scale testing leading to commercial development is undertaken.

Gas atmospheres in the preliminary loading tests on individual pellets will be confined to hydrogen/water vapor mixtures spiked with 3 vol% hydrogen sulfide. Regeneration tests will be limited to gas atmospheres containing air plus nitrogen; the provisional gas atmosphere for the fixed-

¹Turkdogan, E. T. and Olsson, R. G.: "Desulfurization of Hot Reducing Gases with Manganese Oxide Pellets", *Proceedings Third International Iron and Steel Congress* ASM Metals Park, Ohio, 1979, pp.277-288.

bed loading tests was decided upon at METC with the sponsor to be a gas composition simulating the Tampella U gas composition²: 24.33%CO, 5.16%CO₂, 13.19%H₂, 5.35% H₂O, 0.118% H₂S, 5.35% H₂O, balance nitrogen, with the exception that the hydrogen sulfide level will be varied between 1 and 3% to achieve earlier break-through.

PROGRESS TO DATE ON PROGRAM

Overall Observations:

A review of the experimental test plan from the November 16 meeting with the sponsor in Morgantown was presented in Appendix A of the prior Quarterly Report (Issued 12/1/93) and will not be repeated here.

More recently at a meeting held at METC on January 28, 1993, the following observations were made:

- Dr. E. T. Turkdogan in discussing his prior successful tests at the U. S. Steel Research Center compared the relative merit of lime, zinc oxide, and manganese oxide as desulfurizers as expressed in terms of the ratio of water vapor pressure to hydrogen sulfide pressure as a function of temperature. Although zinc-based compounds can attain a higher degree of desulfurization than manganese-based sorbents for a given total hydrogen content of the hot fuel gas, he indicated that over twenty cycles of loading and regeneration he saw no loss of reactivity of manganese-based sorbents when loaded and regenerated at elevated temperatures (700-900°C). Over this range of testing he observed manganese/alumina sorbents increased in reactivity with each cycle of loading, precluding the likelihood of sintering.

Dr. Turkdogan also has re-evaluated the thermodynamic data for the Manganese-Oxygen-Sulfur system, comparing his observations with other investigators. This comparison is presented in Appendix A to this report.

²Tampella U gas also contains 0.111% NH₃ and 1.84% CH₄, which will be disregarded in this study.

- The second observation was made that our prior plan to load our manganese-based sorbents at high temperatures, e. g., 900°C (1652°F) exceeds the temperatures required for combined-cycle operation. Presently the upper limit of turbine operation is 1100°F (593°C). Although Turkdogan did not operate his pellets in loading conditions this low in temperature, we should, in our initial tests, determine whether the reaction kinetics after several loading and regeneration cycles are as good for the manganese-based pellets as those reported with zinc ferrite. If the kinetics are poorer for manganese-based pellets, then the loading temperature can be raised but with some reduction in ultimate level of sulfur which can be removed as compared with zinc-based sorbents.
- As a third observation, upon regeneration, sulfation can be avoided by regenerating at temperatures above 1100°C (2012°F) (See Figure 1). These elevated temperatures can be achieved in practice by allowing the bed to rise in temperature by the exothermic reactions associated with the oxidation of sulfur. Initial regeneration studies will be made at this temperature and the results will be discussed in the next quarterly report.

Current Status of Test Work:

Starting materials:

Chemetals, Inc. is the source of manganese carbonate.

Comilog ore (predominantly MnO_2 from Prince Mfg. Corp.) The purpose of using this material is to determine if the prior studies at U.S. Steel by E. T. Turkdogan in the late 1970's can be reproduced. Reagent grade manganese carbonate from the Chemetals source will be used as the standard against which material to be received from the U. S. Bureau of Mines as a product from their in situ mining project will be compared.

Pelletization:

Additives including Dextrin (5%) and Bentonite (2%), are being employed in a previously documented procedure (Appendix A of the prior Quarterly Report). Induration is being conducted for a 12-hour cycle in air: heating from 25°C to 300°C over a period of 1 hr; heating from 300°C to 400°C over a period of 4 hours (343°C is the decomposition temperature of manganese carbonate); heating from 400°C to 1200°C over a period of 5 hrs; and then holding at 1200°C for two hours; furnace cool overnight to room temperature. The room-temperature crush strength of the pellets has been found to be as high as 42.5 pounds dead weight (on a pellet of 5-8 mm in diameter). BET surface area measurements are pending.

Thermodynamics: The thermodynamics of the Mn-S-O system is being updated via help of our consultant, Dr. E. T. Turkdogan. Preliminary indications are that the theoretical calculations exhibit higher sulfur overpressures than were determined by experiment. (See Appendix A to this report).

Available raw materials:

- A small sample of MnCO_3 : Brought by Mr. R. Ben Slimane from the USBM - Salt Lake Laboratories.
- Manganese Ore obtained from the USBM Twin Cities Laboratories
- Manganous-oxide (MnO) ore obtained from Chemetals in Baltimore (55-83% MnO).
- Ultrafine MnCO_3 (93-95%) obtained from Chemetals.
- MnO_2 Comilog ore (Africa).
- MnO_2 ore (Australia)

(See Tabular data attached for assays on several of the feed stocks).

- Alundum (96.6% Al_2O_3) obtained from Norton Materials.
- Bentonite obtained from Aldrich Chemical Co.
- Dextrin, an organic binder.

Preliminary Results of Pelletization Procedures:

The following are some preliminary data obtained using the Australian ore:

Batch 1-4-1:

- Water content of pellets : 9.95%
- Room Temperature green crush strength : 6.4 lbs
- Induration at $T = 1240^\circ\text{C}$ of 40 pellets : weight loss was 11.30%
- Room temperature crush strength of indurated pellets: 105.5 lbs!

Batch 1-4-2:

- Moisture content of pellets : 6.12%
- Room Temperature green crush strength : 6.0 lbs
- Induration at $T = 1200^\circ\text{C}$ of 27 pellets : weight loss was 11.20%
- Room temperature crush strength of indurated pellets: 55 lbs

These pellets appear to have excessively high crush strengths. If BET measurements are low and also reactivities are low, then lower induration temperatures may be indicated in the preparation of future pellets.

Surface area measurements:

The B. E. T. method is used for the determination of the total area of solids on pellets. The pellets are crushed and an appropriate amount is taken from the size fraction plus 35 minus 20 mesh, in accordance with B. E. T. procedures.

Use of Gas chromatography to measure gas compositions:

The gas chromatograph which is being employed is a Hewlett Packard Model 5890 Series II. It can be used with the provided teflon column and a glass column each packed with Chromosil 310. It has five detector systems: flame ionization, nitrogen/phosphorous, electron capture, thermal conductivity, and flame photometric. The latter system should be able to detect H₂S levels in the off-gases in the range of between 1 and 200 ppm.

Assays of Feedstocks

1) "Moanda" Comilog Ore (African Manganese Dioxide Ore) and "GE" Manganese Dioxide Ore (Australian): Received from: The Prince Manufacturing Company. See subsequent pages for a typical analysis of these two ores.

Typical Chemical Analysis of Ore Feeds

Comilog (African) Ore

Australian Ore

Species	Wt.%	Species	Wt.%
Mn	51.2	Mn	52.8
MnO ₂	77.0	MnO ₂	83.6
MnO	3.36	Al ₂ O ₃	3.4
Al ₂ O ₃	6.01	Fe	2.2
Fe	2.81	SiO ₂	2.8
SiO ₂	2.56	BaO	1.86
K ₂ O	0.71	K ₂ O	1.25
BaO	0.22	Na ₂ O	0.21
TiO ₂	0.22	MgO	0.2
P	0.109	SrO	0.16
Co	0.099	TiO ₂	0.13
CaO	0.08	P	0.06
Zn	0.064	CaO	0.05
MgO	0.06	V	0.03
Ni	0.058	Zn	0.019
Cu	0.05	Co	0.015
CO ₂	0.04	Ni	0.013
Na ₂ O	0.04	Cu	0.008
S	0.019	Pb	0.005
V	0.012	As	0.005
As	0.007	F	0.006
Cr	0.006	Cl	0.005
Mo	0.006	S	0.005
Pb	0.004	Cr	0.003
H ₂ O (bound)	5.16	Mo	0.004
		Sb	0.001
		B	0.001
		Li	0.001
		W	0.001
		Cd	0.0005
		H ₂ O (bound)	3.4

2) Alundum Fepa F, Size 600, Code 7102
Received from: Norton Industrial Ceramics Corporation

Typical Chemical Analysis:

Species	Al ₂ O ₃	TiO ₂	SiO ₂	Fe ₂ O ₃	CaO	MgO	S	K ₂ O
Wt. %	96.60	2.60	0.60	0.20	0.10	0.40	0.02	0.02

3) Manganese Carbonate: Received from Chemetals, Inc.

This product contains approximately 93-95% MnCO₃; no typical analysis is available at the present time.

4) Manganous Oxide (MnO) Ore, Industrial Grades: Received from Chemetals, Inc.

This product contains approximately 60% manganese.

Ingredient	Approximate %
Manganese Oxide	55 - 83
Manganese Tetroxide	75 - 85
Iron as Iron Oxide	4, max.
Silica as Silicon Oxide	5, max.
Aluminum Dioxide	8, max.
Barium as Barium Compounds	4, max.

Preliminary TGA Testing for Reactivity:

Preliminary experimental results using gases containing only H_2 for the reduction gas and H_2 containing 3% by volume H_2S are encouraging. Starting with Australian Ore (See previous table for assay,) pellets were made and subjected to induration in air atmosphere which converts the MnO_2 to Mn_3O_4 . Two tests on indurated pellets are reported here, the first a pellet weighing 122.1 mg (Run 2-10-1) is a loading test at $700^\circ C$ and the second on a pellet weighing 162.5 mg is a loading test at $900^\circ C$.

Figure 1 shows the ratio of weight at any time to starting weight W/W_o in the TGA unit plotted as a function of time in minutes. The decline in weight over the first 30 minutes for Run 2-10-1 and for 40 minutes for run 1-15-1 is during the reduction stage (H_2 without H_2S). Hydrogen sulfide was added after these periods which were arbitrarily taken as the time subsequent to which very little measured change in weight was observed.

Shown on this figure is a dashed line corresponding to complete reduction of the starting Mn_3O_4 to MnO (Note that although the starting state of manganese is the compound MnO_2 , upon induration in air, at $1200^\circ C$ MnO_2 is reduced to Mn_3O_4 . See Figure 1A.) Also shown is a higher dashed line corresponding to the weight ratio which would pertain to complete conversion of the manganese oxide to the sulfide. After the addition of sulfur to the hydrogen, a sharp upward slope is shown corresponding to the sorption of sulfur and desorption of oxygen (the former having twice the atomic weight of the latter). The tests were arbitrarily discontinued at 100 minutes at which time the relative sorption of the pellet can be determined. For the lower temperature test ($700^\circ C$) sorption is approximately 49% complete; whereas, for the higher temperature test ($900^\circ C$), sorption is 81% complete.

Figure 1 Stability Diagram for the System Mn-S-O

Figure 2: Thermogravimetric Analysis of Pellets made from Australian Ore in Hydrogen followed by Hydrogen plus 3% Hydrogen Sulfide Atmospheres at 700°C and at 900°C

Figure 3: Stability Diagram of Mn-O System as a Function of Oxygen Potential (P_{CO_2}/P_{CO}) and Temperature.

APPENDIX A

Revision of Thermodynamic Data Mn-O-S System

by

E. T. Turkdogan

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REPORT 1 TO UNIVERSITY OF MINNESOTA
PROJECT DOE/DE-AC21-92 MC 2946

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RE-ASSESSMENT OF FREE ENERGY
DATA FOR MnO, MnS AND MnSO₄

Introduction

I have been aware for some time now that there are differences in the thermochemical tables from one set of compilation to another. Apparently it is not unusual to find differences of 5 to 15 kJ/mol in the standard free energies of formation of metal oxides, sulfides and other compounds. Because of such variations in the compiled free energy data, the estimated equilibrium constants of reactions will be uncertain by factors of two or three. Such level of uncertainty is not acceptable in the assessment of the equilibrium states of reactions in an industrial process.

In relation to the DOE sponsored project on the hot coal gas desulfurization using manganese base sorbents, the available thermochemical and reaction equilibrium data are re-assessed. The results are given in this report.

The following symbols and notations are used in the text and equations.

ΔG_{MX}° = The standard free energy of formation of compound MX from its elements in their standard states.

ΔG_r = The free energy change accompanying the reaction.

< > = Solid reactants.

() = Gaseous reactants.

MnO/MnS Equilibrium

Of particular importance to the desulfurization of hot reducing gases with MnO and its regeneration from MnS (spent sorbent), we should first re-assess the equilibrium sulfur and oxygen potentials for the reaction

Three independent studies have been made.

- (a) Using the emf method, Larson and Elliott¹ measured the state of equilibrium for the reaction at temperatures of 1021 to 1379 K.

$$\Delta G_r = 465,420 - 78.20T \quad \text{J/mol} \quad (3)$$

- (b) Turkdogan et al.² measured the equilibrium gas compositions for the formation of MnS from MnO by reacting the oxide with H_2 - H_2S - H_2O mixtures at temperatures of 973 to 1473 K.

$$\Delta G_r = -63,760 + 5.94T \quad \text{J/mol} \quad (5)$$

- (c) Using the emf method, Huang and Rosén³ recently measured the states of various reaction equilibria in the system

Mn-S-O. For the MnO/MnS reaction at temperatures of 914 to 1300 K.

$$\Delta G_r = 336,732 + 762.32T - 236.83T \log T \quad (7)$$

Combining these values of ΔG_r with the ΔG° values for SO_2 , H_2O and H_2S , we obtain the ΔG_r values for reaction (1). These are plotted in Fig. 1. For almost all reactions, the ΔG_r is practically a linear function of temperature. The results of Huang and Rosén (curve c) are not consistent with the expected ΔG_r -T relation.

The lines d and e are derived from the following compilation of the free energy data:

- (d) From the thermochemical tables compiled by Barin et al.^{4,5} for MnO and MnS.
- (e) Using the $\Delta G_{\text{MnO}}^\circ$ data compiled by Coughlin⁶ together with $\Delta G_{\text{MnS}}^\circ$ from the compilations by Cooper and Scarpiello⁷ and by Pankratz and King⁸.

The average of the lines d and e is taken for ΔG_r at temperatures of 900-1500 K.

$$\Delta G_r = 110,730 - 9.08T \text{ J/mol} \quad (8)$$

Combining this with $\Delta G_{\text{MnO}}^\circ$ compiled by Coughlin

$$\Delta G_{\text{MnO}}^{\circ} = -384,840 + 73.14T \text{ J/mol} \quad (10)$$

we obtain the following recommended value for $\Delta G_{\text{MnS}}^{\circ}$:

$$\Delta G_{\text{MnS}}^{\circ} = -274,110 + 64.06T \text{ J/mol} \quad (12)$$

Mn₃O₄/MnSO₄ Equilibrium

Several studies have been made of the Mn₃O₄/MnSO₄ equilibrium by determining the equilibrium dissociation partial pressures of SO₂ and O₂ in the reaction

As is seen from the plot in Fig. 2, the results of different investigations are in general accord with one another. As noted by Skeaff and Espelund⁴, MnSO₄ has two crystalline forms:

α-phase below 849°C and β-phase above 849°C.

The average of all the data may be represented by the following equations for temperatures of 900 to 1300 K.

$$\log p_{\text{SO}_2} (p_{\text{O}_2})^{1/2} = - \frac{15,625}{T} + 11.888 \quad (14)$$

$$\Delta G_r = 299,160 - 227.61T \text{ J/mol} \quad (15)$$

Mn₃O₄/MnO Equilibrium

The equilibrium measurements made by Hahn and Muan¹¹ and by Schwerdtfeger and Muan¹² are summarized by the following equation for temperatures of 1200 to 1813 K (mp Mn₃O₄).

$$\langle \text{Mn}_3\text{O}_4 \rangle = 3\langle \text{MnO} \rangle + \frac{1}{2}(\text{O}_2) \quad (16)$$

$$\Delta G_r = 232,210 - 116.98T \text{ J/mol} \quad (17)$$

Equilibrium H₂S/H₂O Ratio

in Desulfurized Hot Coal Gas

Combining ΔG_r in equation (8) with $\Delta G^\circ_{\text{H}_2\text{S}}$ and $\Delta G^\circ_{\text{H}_2\text{O}}$ values gives

$$\langle \text{MnS} \rangle + (\text{H}_2\text{O}) = \langle \text{MnO} \rangle + (\text{H}_2\text{S}) \quad (18)$$

$$\Delta G_r = 45,120 + 4.06T \quad (19)$$

$$\log \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2\text{O}}} = - \frac{2357}{T} - 0.212 \quad (20)$$

Using this recommended equilibrium relation, the following estimates are made of the equilibrium H₂S contents of the desulfurized gas, depending on temperature and H₂O content of the hot coal gas.

<u>Temperature, K</u>	<u>%H₂O</u>	<u>ppm (vol.) H₂S</u>
1200	2	54
"	10	270
1300	2	188
"	10	940

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Fig. 1 Experimental and calculated free energy data for the reaction
 $\text{MnO} + \frac{1}{2}(\text{S}_2) = \text{MnS} + \frac{1}{2}(\text{O}_2)$

Average of lines d and e is recommended

$$\Delta G_r = 110,730 - 9.08 T \text{ J/mol}$$

$p_{SO_2}(p_{O_2})^{1/3}, \text{atm}^{4/3}$

Fig. 2 Experimental data for equilibrium constant

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January 6, 1993

Dear Malcolm,

Thank you for your letter of December 29 enclosing a letter from your graduate student Rachid Ben Slimane. His calculations are correct and his comments are well taken. In fact, I was planning to write to you for a few minor corrections in my Report 1 and to discuss the point that was raised by Slimane.

First, let me take care of the corrections. Slight corrections have been made on the positions of the lines d and e in Fig. 1. Equations 8 and 12 should be as follows.

$$\Delta G_p = 111,130 - 9.06T \quad (8)$$

$$\Delta G_{MnS}^\circ = - 273,670 + 64.08T \quad (12)$$

The line d is from references 6, 7 and 8; the line e from 4 and 5.

It should be noted that ΔG_{MnO}° from the thermochemical compilation of Barin and Knacke is the same as originally assessed by Coughlin². The difference in the positions of the lines d and e in Fig. 1 is due to a difference of about 8.5 kJ between the ΔG_{MnS}° values given in references 6 and 7(8). It should be noted that the thermochemical data on MnS given in the compilation by Barin et al⁵

is in fact based on the previous compilation made by K.C. Mills¹.

In the re-assessment of experimental results of different investigators, coupled with the thermochemical calculations, one has to be impartial and unbiased. For that reason, my initial thought was to take the average of the lines d and e in Fig. 1 as given in my Report 1. However, upon further reflection, I felt that perhaps we should give more credence to the line e which is in the middle range of the experimental results from two independent investigations. The equation for line e is

$$\Delta G_r = 106,420 - 8.64T \quad \text{J/mol}$$

which is of course the sum of $\Delta G_{\text{MnO}}^\circ$ and $\Delta G_{\text{MnS}}^\circ$

$$\Delta G_{\text{MnO}}^\circ = - 384,340 + 73.14T \quad \text{J/mol} \quad (\text{Coughlin})$$

$$\Delta G_{\text{MnS}}^\circ = - 278,420 + 64.50T \quad \text{J/mol} \quad (\text{Mills}).$$

Now, combining the equation for line e with equations for $\Delta G_{\text{H}_2\text{O}}^\circ$ and $\Delta G_{\text{H}_2\text{S}}^\circ$ gives

¹ K.C. Mills, "Thermodynamic Data on Inorganic Sulphides, Selenides and Tellurides", Butterworth Pub., 1974.

$$\Delta G_r = - 49,430 - 3.36T \quad \text{J/mol}$$

$$\log \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{S}}} \right) = \frac{2582}{T} + 0.175 \quad (1)$$

which differs somewhat from the results of the earlier measurements made by Olsson and Vinters², thus

$$\log \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{S}}} \right) = \frac{3330}{T} - 0.310 \quad (2)$$

The results obtained from the packed bed experiments of Olsson in Fig. 13 of our paper* are compared in the enclosed diagram with the dotted line for Equ.1. I am inclined to accept Equ. 1 in preference to Equ. 2.

However, in view of the importance of the equilibrium ratio $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{S}}$ in hot coal gas desulfurization with $\text{MnO}(\text{Al}_2\text{O}_3)$, I suggest that a few equilibrium measurements be made using the experimental technique employed by Rosenqvist** in determining the reaction equilibrium

I would be interested to know the outcome of Slimane's experimental work with the $\text{MnO}(\text{Al}_2\text{O}_3)$ pellets.

* E.T. Turkdogan and R.G. Olsson, Proc. 3rd Inter. Iron and Steel Congress, ASM, 1979, pp. 277-288.

** T. Rosenqvist, Trans. AIME, 1952, 191, 535-540.

Yours sincerely,

Tugrul Turkdogan

Fig.1 Experimental and calculated free energy data for the reaction
 $\langle \text{MnO} \rangle + \frac{1}{2} (\text{S}_2) = \langle \text{MnS} \rangle + \frac{1}{2} (\text{O}_2)$

Fig. 13--Comparison of H_2O/H_2S ratios from packed bed experiments with the equilibrium lines for Reaction $<MnO> + (H_2S) = <MnS> + (H_2O)$

----- Equ. 1
 _____ Equ. 2

temperature range 1800 to 2000 K.

$$\Delta G_{\text{MnO}}^{\circ} = - 360,170 + 65.62T \quad \text{J/mol} \quad (32)$$

REACTION EQUILIBRIA IN THE
SOLID Mn-S-O SYSTEM

An interest has been shown in some of the R & D laboratories on the possible use of the MnO based absorbents to desulphurise hot coal gases, as an extension of the earlier work that was done by Turkdogan and Olsson¹⁹. In the context of the present study, an assessment will be made of the previous experimental data on reactions involving solid MnO, MnS and MnSO₄ in relation to those calculated from the thermochemical tables.

Four independent studies have been made of reactions involving gases, MnO and MnS.

- (a) Using the emf method, Larson and Elliott²⁰ measured, over the temperature range 1021-1379 K, the state of equilibrium for the following reaction.

$$\Delta G_r = 465,420 - 78.20T \quad \text{J/mol} \quad (34)$$

- (b) Using the emf method, Huang and Rosen²¹ have recently measured the states of various reaction equilibria in

the Mn-S-O system. For reaction in Equ. 33, the following ΔG_r values were obtained over the temperature range 914 to 1300 K.

$$\Delta G_r = 336,732 + 762.32T - 236.83T \log T \quad \text{J/mol} \quad (35)$$

- (c) Using 10 mm dia. MnO pellets stacked in a packed-bed reactor (40 mm dia. and 190 mm deep), Turkdogan and Olsson¹⁹ studied the sulphidation of MnO with the H₂S-H₂ mixtures (with 1.1 to 3.3% H₂S) flowing through the bed at the rate of 3 l/min. The residual concentration of H₂S in the exhaust gas was measured periodically. After the initial 40 minutes of reaction time, the H₂S content of the exhaust gas reached a steady state, indicating the establishment of MnO/MnS equilibrium in the packed bed. Noting that the amount of water vapor in the exhaust gas is equal to the quantity of H₂S reacted, the partial pressure ratio $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{S}}$ in the exhaust gas is readily derived from %H₂S in the exhaust gas for the steady state condition and the composition of the ingoing H₂S-H₂ mixture. In a different type of experiment, using 50 mg MnO samples, Turkdogan et al.²² measured the equilibrium gas compositions for the formation of MnS from MnO by reacting the oxide with H₂-H₂S-H₂O mixtures of known composition at temperatures of 973 to 1473 K.

(d) In an earlier work done by Dewing and Richardson²³ on the MnO/MnS equilibrium, the method used was to circulate $H_2 + H_2S$ through a water vapour saturator and over a heated mixture of MnO and MnS. The H_2S content of the circulating gas was measured continuously by incorporating radioactive-sulphur³⁵ in the gas mixture and introducing GM counter in the gas circuit.

The equilibrium constants p_{H_2O}/p_{H_2S} , obtained from the above mentioned studies, for the reaction

are plotted in Fig. 7. These two sets of equilibrium data may be represented by the following equations:

Dewing and Richardson data²³:

$$\log \left(\frac{p_{H_2O}}{p_{H_2S}} \right) = \frac{2016}{T} + 0.218 \quad (37)$$

Turkdogan et al. data^{19,22}:

$$\log \left(\frac{p_{H_2O}}{p_{H_2S}} \right) = \frac{3266}{T} - 0.288 \quad (38)$$

The line for Equ. 44 in Fig. 7 is discussed later.

By combining the experimental data on ΔG_r for MnO/MnS reactions in the foregoing studies (a to d), with the ΔG_{MX}° values for SO_2 , H_2O

and H_2S , we obtain the G_r values for the reaction

These ΔG_r values from four independent studies are plotted in Fig. 8.

The lines e and f are derived using the $\Delta G_{\text{MnO}}^\circ$ data assessed by

Coughlin¹⁷

$$\Delta G_{\text{MnO}}^\circ = - 384,840 + 73.14T \quad \text{J/mol} \quad (40)$$

and two different assessments of the $\Delta G_{\text{MnS}}^\circ$ values:

- (e) $\Delta G_{\text{MnS}}^\circ$ values assessed by Cooper and Scarpiello²⁴ and by Pankratz and King²⁵.
- (f) $\Delta G_{\text{MnS}}^\circ$ values derived from the thermodynamic data on inorganic sulphides, selenides and tellurides compiled by Mills²⁶.

There is a considerable spread in the experimental and calculated values of ΔG_r for the reaction in Equ. 39. The experimental results of Dewing and Richardson give the highest ΔG_r values. The curve b from the experimental work of Huang and Rosén is unrealistic, because within the temperature range considered, ΔG_r is expected to be a linear function of temperature.

In my assessment of the situation, I am inclined to give more credence to the line f which is in the middle range of the experimental results from two independent investigations using entirely different experimental techniques. The equation for line f is

$$\Delta G_r = 106,900 - 9.18T \quad \text{J/mol} \quad (41)$$

which is of course the sum of $\Delta G_{\text{MnO}}^\circ$ (Equ. 40) and $\Delta G_{\text{MnS}}^\circ$ from the compilation of Mills, for the range 298 to 1517 K.

$$\Delta G_{\text{MnS}}^\circ = - 277,940 + 63.96T \quad \text{J/mol} \quad (43)$$

Combining Equ. 41 with equations for $\Delta G_{\text{H}_2\text{S}}^\circ$ and $\Delta G_{\text{H}_2\text{O}}^\circ$ gives the following equilibrium relation for reaction in Equ. 36.

$$\log \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{S}}} \right) = \frac{2557}{T} + 0.204 \quad (44)$$

This equation is used for the line drawn in Fig. 7.

There is another evidence from the results of an entirely different experiment which supports the reliability of Equ. 43 for the standard free energy of formation of MnS. In the early 1950's, Turkdogan et al.²⁷ studied the solubility of sulphur in solid iron and iron-manganese alloys. The equilibrium partial pressure ratios $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ obtained for the reaction

are reproduced in the second column of Table 2. The ΔG_r values obtained from these experimental data are given in the third column. Combining these ΔG_r values for reaction in Equ. 45 with $\Delta G_{\text{H}_2\text{S}}^\circ$ and $\Delta G_{\text{Mn}}^\circ = - 38.16T \quad \text{J/mol}$ for the ideal solution of Mn in solid iron at 1% Mn gives the $\Delta G_{\text{MnS}}^\circ$. It is seen that $\Delta G_{\text{MnS}}^\circ$ thus derived from the experimental data on the MnS solubility in solid iron agree well enough with those of Equ. 43.

$$\Delta G_{MnO}^{\circ} = - 360,170 + 65.62T \text{ J/mol (1800 to 2000 K)}$$

$$\Delta G_r = 106,900 - 9.18T \text{ J/mol (900 to 1500 K)}$$

$$\Delta G_r = - 48,950 - 3.90T \text{ J/mol (900 to 1500 K)}$$

$$\Delta G_{MnO}^{\circ} = - 384,840 + 73.14T \text{ J/mol (298 to 1517 K)}$$

This is from the compilation by Coughlin¹⁷.

$$\Delta G_{MnS}^{\circ} = - 277,940 + 63.96T \text{ J/mol (298 to 1517 K)}$$

This is from the compilation by Mills²⁶.

$$\Delta G_r = 299,160 - 227.61T \text{ J/mol (900 to 1300 K)}$$

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Table 2. The standard free energy of formation of MnS derived from data on MnS solubility in solid iron is compared with the thermochemical data

%Mn	$(p_{H_2S}/p_{H_2}) \times 10^4$	ΔG_r	$\Delta G_{MnS}^\circ, \text{kJ/mol}$	
		kJ/mol	From G_r	From Equ.43
1200°C				
0.37	4.40	- 106.85	- 180.18	- 183.73
1.07	1.52			
1.30	1.25			
1335°C				
0.37	10.85	- 104.61	- 176.72	- 175.09
0.70	5.70			
1.30	3.10

Fig. 7 Comparison of experimental data on reaction equilibrium $\text{MnO} + (\text{H}_2\text{S}) = \text{MnS} + (\text{H}_2\text{O})$ with that calculated from the compiled thermochemical tables, Equ. 44.

Fig. 8 Experimental and calculated free energy data for the reaction
 $\langle \text{MnO} \rangle + \frac{1}{2}(\text{S}_2) = \langle \text{MnS} \rangle + \frac{1}{2}(\text{O}_2)$

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