

CHAPTER III: THERMODYNAMIC COMPARISON OF SEVERAL SORBENT SYSTEMS FOR HOT COAL-DERIVED FUEL GAS DESULFURIZATION

This chapter is a slightly edited version of a paper published in the American Chemical Society Journal "Energy & Fuels."

Acknowledgement. We express our appreciation to the Department of Energy, Morgantown Energy Technology Center, under Contract DE-AC21-92MC29246 and also the U.S. Bureau of Mines, Twin Cities Research Center, Grant USDI-BM/C0299002-Mod.3 for providing support for this study.

Reprinted with permission from *Energy & Fuels* 1993, 7, 602-609. Copyright 1993 American Chemical Society.

Thermodynamic Comparison of Several Sorbent Systems for Hot Coal-Derived Fuel-Gas Desulfurization

M. T. Hepworth,^{*} R. Ben-Slimane,^{**} and S. Zhong^{**}

*Department of Civil and Mineral Engineering, University of Minnesota,
500 Pillsbury Drive, S. E.; Minneapolis, MN 55455-0220*

Received October 2, 1992. Revised Manuscript Received July 1, 1993[⊙]

A systematic approach toward the evaluation of the behavior of single-metal sorbents for removing sulfur from hot coal-derived fuel-gases is developed from thermodynamic considerations. A procedure is developed (and represented in graphical form) to compare a range of metal-based sorbents (Fe, Ni, Mg, Ca, Mn, Cu, and Zn) with respect to their ability to remove sulfur from fuel gases produced over a range of equivalence ratios. The examples which are given are for a specific Illinois No. 6 coal; however, the calculation method can readily be extended for any coal and other sorbent, such as mixed-metal systems using referenced standard computer programs.

^{*} Author to whom correspondence should be addressed.

^{**} Research Assistants

• Abstracts published in *Advance ACS Abstracts*, August 15, 1993.

3.1 Introduction

The U. S. Department of Energy has been exploring several approaches to clean coal combustion to produce electrical energy. These approaches range from single-use sorbent additions to slagging gasifiers during combustion to the passage of hot fuel gases through beds of regenerable sorbents.^{1,2,3,4} In the latter instance, these sorbents are invariably oxides which are converted to sulfides during a sulfur "loading" stage under reducing hot fuel gas conditions and then regenerated by oxidation of the sulfides to oxides and a concentrated byproduct stream of sulfur dioxide. For single-use sorbents, the reagents which are of practical consideration must be inexpensive and, as a result, are confined to calcium- or magnesium-based oxides; however, recently iron-based sorbents have been considered.⁵ In this paper single-metal oxide/sulfide systems are discussed as potential desulfurization sorbents. A method of evaluating the ultimate desulfurizing power of sorbents and their capabilities for regeneration is shown from entirely thermodynamic considerations. In addition, conditions quantifying the extent of desulfurization, in terms of the percentage of sulfur removal and H₂S terminal levels, are mapped as a function of partial pressures of sulfur and oxygen in the cleaned gas and a wide range of temperature values. This procedure can easily be extended to mixed-metal sorbent compounds and solutions, provided the thermodynamic data are known.

Previously, Westmoreland *et al.*⁶ screened the high-temperature desulfurization potential of 28 solids, primarily metal oxides, based on thermodynamic considerations alone. This earlier work, which was subsequently followed by kinetic studies,⁷ was based on a free energy minimization method to determine equilibrium sulfur removal and solid compound stability. The purpose of this paper is to demonstrate the wide applicability of a thermodynamic program developed by Zhong and Hepworth,⁵ and that of the STEPSOL software package,⁸ a chemical equilibrium program for the simulation of semibatch metallurgical reactors on an IBM-PC or compatible. STEPSOL is capable of handling systems up to 14 elements, 84 species, and 19 phases through up to 24 steps and is thus valuable in the calculation of chemical equilibria in complex systems.

3.2 Analytical Approach

In order to illustrate the thermodynamic method used in this analysis, a typical high-sulfur Illinois No. 6 coal has been used as the coal producing a gaseous product. The assay of this coal is given in Table 3.1. The gaseous species considered include N₂, CO, CO₂, H₂O, H₂, H₂S, S₂, COS, SO₂, SO₃, O₂, S, S₄, SO, CS, CS₂, NO, NO₂, CH₄, and NH₃. For a system in which coal gases are equilibrated with a combination of two solid phases (for example metal oxide and metal sulfide), the Gibbs phase rule predicts the number of degrees of freedom as $F = C + 2 - P$, where C is the number of components and P is the number of phases (three in our analysis, gas plus two solids). The components are metal, oxygen, and sulfur. Most of the examples which will be considered are for a three-phase, three-component system. For such a system, the number of degrees of

freedom (F) is two, and therefore at a fixed total pressure of 1 atm, the chemical potential of oxygen and sulfur are uniquely determined at a given temperature. The two components of sulfur and oxygen are most conveniently represented by the logarithms of their partial pressures.

Table 3.1 Analysis of Illinois No. 6 Coal Used in Calculations, Basin Coal IBC-107 (Herrin)

| constituent | % by weight |
|---------------------|-----------------------------|
| carbon | 67.87 |
| hydrogen | 5.0 |
| nitrogen | 1.2 |
| total Sulfur | 3.87 |
| oxygen | 10.56 (not included in ash) |
| ash | 11.5 |
| total | 100.0 (dry basis) |
| moisture | 9.3 |
| gross heating value | 28415 kJ/kg |

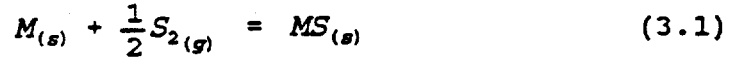
Figure 3.1, however, shows the oxygen potential which results from establishing a given equivalence ratio for the single-phase gas composition (absence of any solid phase) resulting from gasification of the referenced coal (at a series of fixed temperatures and 1 atm pressure). This figure defines the gasification conditions of equivalence ratio as a function of oxygen potential and temperature for the above-referenced coal by a method described in the next section of this paper. This figure shows that at a given equivalence ratio, the product gas becomes less reducing with increasing temperature. This figure also shows that higher equivalence ratios are required at higher temperatures to achieve the same oxygen pressure. For example, an equivalence ratio of almost 3 is required to establish an oxygen pressure of 10^{-16} at 1450 °C. This would be equivalent to burning coal to produce only hydrogen and carbon monoxide, without carbon dioxide or water vapor, as is usually the case for gasification aimed at the production of synthesis gas.

Figures 3.2a through 3.2c give the calculated concentrations of the majority of sulfur species as determined by standard computer programs (e.g., SOLGASMIX). In examination of these figures, one can see that for equivalence ratios associated with gasification (i.e. > 1), oxidized sulfur in the species SO_2 becomes negligible with respect to lower-valent sulfur in COS and H_2S , the latter being the majority species as shown. Because of the presence of hydrogen in the coal, H_2S concentrations are very much larger than the species S_2 . Desulfurization with sorbents, then, is essentially a process of removal of the species H_2S from the

gas phase. Of course, as H_2S is removed, the other minority species equilibrate in the gas phase and also are proportionately reduced.

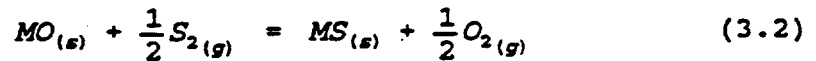
Figure 3.3 is a predominance equilibrium diagram for a hypothetical metal-sulfur-oxygen system (M-S-O) at a given temperature, as a function of the oxygen and sulfur partial pressures (the two components chosen for the analysis). According to this figure, desulfurization can be accomplished by two possible reactions, depending on whether the elemental metal or the oxide is stable.

If the metal is stable, desulfurization may be represented by reaction (3.1)

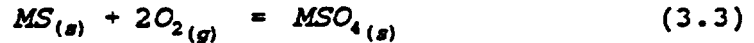


It must be noted, however, that metallic sorbents cannot usually be used for desulfurization, primarily because of the difficulty of converting the sulfide to the metal for recycle, which is the fundamental reason why sulfides are first converted to oxides prior to smelting in metallurgical processing.

If the oxide is stable, desulfurization may be represented by reaction 2



Unfortunately, the choice of oxides is also limited because of the reduction of some oxides during the desulfurization of hot reducing gases. Figure 3.3 shows that the following reactions are also possible. They are undesirable for the sulfidation as well as the regeneration process steps.



With these restrictions in mind, five types of equilibria involving elemental metal (M), metal oxide (MO), metal sulfide (MS), and metal sulfate (MSO_4) are explored in the subsequent analysis. They are elemental metal/metal oxide (M/M_xO_y), metal sulfide/metal sulfate (M_xS/MSO_4), elemental metal/metal sulfide (M/M_xS), metal oxide/metal sulfide (M_xO/M_xS), and metal oxide/metal sulfate (M_xO/M_xSO_4).

3.3 Complex Chemical Systems

Calculation of chemical equilibria in complex systems requires computer methods because of their complexity when more than a small number of reactions must be considered. Calculations require solution of simultaneous, nonlinear equations which are constrained by the mass balance of the system and would, if

conducted by hand calculator require multiple iterations. In recent years the program SOLGASMIX⁹ has been widely used in the calculation of chemical equilibria, including the calculation of predominance diagrams.^{10,11,12,13} The program uses Lagrange's method of undetermined multipliers coupled with the method of steepest descent to find the minimum free energy of a constrained system, which is, by definition, the equilibrium composition. SOLGASMIX is the basis for the FACT EQUILIB program,¹⁴ as well as the CHEMIX program of CSIRO's (Commonwealth Scientific and Industrial Research Organization) THERMODATA¹⁵ system.

Flynn *et al.*¹⁶ have coupled these programs to formulate a powerful yet easy-to-use equilibrium program package which is suitable for use with IBM personal computers or compatibles. STEPSOL was written to model multistep, semibatch reactors for conditions in which equilibrium is reached in each step. This menu-driven system includes an interactive editor which simplifies the work of typing the data needed by the calculation module. In addition to processing data from compounds, it also includes activity models for solutions including the Bale Pelton Interaction Parameter model,¹⁷ the regular solution model, subregular three-suffix and four-suffix Margules models, the ideal model, and free-form entry model.¹⁸

Based on an iterative approach developed by Rao,¹⁹ Zhong and Hepworth⁵ developed an interactive computer program which permits coal assays to be entered as variables as well as the temperature of the system, total pressure, moisture content, oxygen partial pressure, and sulfur partial pressure. The program output includes the gas phase composition, SO₂ emission concentration, percentage of sulfur removal, NO₂ emission concentration, and equivalence ratio, which can be expected under equilibrium conditions upon gasification of a given coal, followed by desulfurization of the product fuel-gas. (The equivalence ratio is a means of expressing the fuel-to-air ratio, which is defined as the actual amount of fuel expressed as a decimal ratio of the stoichiometrically correct amount of fuel²⁰.) The results reported in this paper can be obtained using either STEPSOL or this program, provided the same thermodynamic data base is used.

3.4 Evaluation of Degree of Desulfurization for Several Metal Sorbent Systems

For the analysis which follows, only thermodynamic considerations are taken into account. Reagent cost, physical stability of substrates, fusion, kinetics, and inherent regenerability based upon physical stability are separate factors which are not addressed here. These factors, however, must be taken into consideration prior to making the ultimate choice among candidate sorbent systems. The purpose of this analysis is to provide a format for analysis of the chemical stability of metal oxide sorbents. The thermodynamic databases used in the following figures are referenced below.^{21,22,23,24,25,26}

In this analysis the significance of the remaining diagrams will first be developed, and then two examples will be given to illustrate the sequence of steps required to fix the optimum equivalence ratio required to desulfurize a given coal-

derived fuel gas. The diagrams are standardized by writing the reactions in terms of 1 mol of oxygen or sulfur gas. This procedure enables comparisons to be made on the same molal basis.

3.5 Graphical Procedure

In Figure 3.4, the phase stability for nine metal oxides (iron and manganese oxides in two forms MO and M_3O_4 , where M designates elemental metal) is shown as a function of oxygen partial pressure and temperature. Each line represents a boundary above which the metal oxide is stable. This diagram is useful in the prediction of metal or oxide stability during the sulfidation stage.

In Figure 3.5, the stability of the sulfate with respect to the sulfide is shown in terms of oxygen pressure and temperature. For example, for manganese sulfate to be stable, oxygen pressures above the middle line on the diagram would be required; below that line, the sulfide would be stable. This diagram is useful in the assessment of sulfide or sulfate stability during the sulfidation or regeneration stages.

Figure 3.6 shows the standard Gibbs free energy of formation of sulfides from sulfur and the metal as a function of temperature. The sulfur pressure can readily be determined from the Gibbs free energy by the equation $\ln P_{S_2} = (1/RT)\Delta G^\circ$. From this relationship, one notes that along the ordinate, less negative Gibbs free energies of formation are directly related to increasing sulfur partial pressures. Therefore the analysis is similar to that in Figure 3.4 for the metal/metal oxide equilibrium. The usefulness of such a representation, which employs the free energy instead of the sulfur partial pressure, will be pointed out later.

Figure 3.7 compares the relative stability of sulfide with oxide in a plot similar to Figure 3.6. The sulfide is stable above the line and the oxide below the line. Accordingly, the most stable sulfide shown, compared with the oxide, is copper sulfide, whereas, the least stable sulfide compared with the oxide is magnesium sulfide. Equilibria for CaO/CaS and MnO/MnS are shown approximately midway in the diagram and cover the entire temperature range studied. The diagram shows that the oxide phases are generally more stable than the sulfide except for copper. For the system $Fe-O-S$ stoichiometric compounds FeO and FeS have no practical significance since this system contains a melt having a wide range of compositions; i. e., sulfur has a solubility range within the melt $Fe-O-S$.²⁷

Figure 3.8 compares the stabilities of sulfate with oxide systems with the sulfide being stable above the line of each equilibrium shown. Higher (less negative) values of the standard Gibbs free energy change occur for less stable sulfates (top of diagram). This figure is especially useful in predicting whether the oxide or sulfate is stable during regeneration of the loaded (spent) sorbent.

Figure 3.9 is a composite representation of Figures 4-8 in which the quantity P_i on the right-hand side of the diagram represents one of the three terms as shown in the legend. For example, for $P_i = P_{S_2}/P_{O_2}$, which corresponds

to a metal oxide/metal sulfide equilibrium, each slanting line is drawn as a function of temperature at the various values indicated on the right-hand side and top of diagram. A ratio of unity, in this example, along a line passing through an ordinate value of zero, would occur for the situation in which the metal sulfide and the metal oxide have an equal stability.

3.6 Example 1

Again making reference to the previously-described Illinois No. 6 coal which is subject to gasification at a equivalence ratio of 1.05 at 800 °C., removal of 95% of the sulfur from the fuel gas at 1 atm total pressure is desired. Reference at 800 °C to Figure 3.1 shows that for an equivalence ratio of 1.05, the oxygen pressure is approximately 10^{-15} atm. Figure 3.10a indicates that for 95% sulfur removal and for P_{O_2} having a value of 10^{-15} , the partial pressure of sulfur, P_{S_2} , is fixed at approximately $10^{-6.15}$ atm. Providing hydrogen sulfide (H_2S) is the only sulfur-bearing species (an excellent approximation as previously established in Figure 3.2a), Figure 3.10b shows that the sulfur content of the cleaned gas corresponds to somewhat less than 200 ppm. Inspection of Figure 3.4 shows that the phase combinations NiO/Ni, Cu_2O/Cu , and MnO/Mn_3O_4 all exhibit oxygen partial pressures greater than this requirement. Consequently, the metal oxides Mn_3O_4 , Cu_2O , and NiO will be reduced to MnO, Cu, and Ni, respectively, and therefore are not suitable as sulfur acceptors under these conditions. On the other hand, the rest of the metal oxides shown in Figure 3.3 would be suitable, i.e. thermodynamically stable.

It must be noted that this example was predicated upon hydrogen sulfide gas (H_2S) being the only sulfur species. As a more exact approach, Figures 10-13, however, are based upon calculations made upon the Illinois No. 6 coal in Table I in which all sulfur-bearing species, as indicated earlier, are taken into account. During the process of gasification, sulfur in the coal is converted predominantly to H_2S . These figures are calculations at the temperatures shown (ranging from 800 to 1400 °C) on plots of sulfur vs oxygen pressure (both in atmospheres), all at a total pressure of 1 atm. The curves (part a) represent lines of equal percentage of sulfur removal, thus quantifying the extent of desulfurization achieved. The curves (part b) represent lines of constant ppm H_2S in the cleaned gas as a function of O_2 and S_2 partial pressures.

A comparison is made between Figures 10a and 13a (800 and 1400 °C). The range of oxygen partial pressures below the 95% sulfur removal line is wide for the higher temperature and very limited for the lower temperature. Reference to Figure 3 shows that in order to achieve such a high degree of desulfurization, operation must be restricted to equivalence ratios ranging for the lower temperature (800 °C) from approximately 1.0 to 1.1 and for the higher temperature (1400 °C) from 1.2 to 3.0. Upon examination of Figure 3.13a, one notes that at higher oxygen pressures ranging up to 10^{-8} atm, the range of satisfactory desulfurization is wide; however, above this pressure, there is a rapid loss of desulfurizing capability. An examination of the above Figures shows that 95% sulfur removal requires a sorbent system which exhibits equilibrium sulfur

partial pressures below approximately $10^{-6.5}$ atm at both temperatures (800 and 1400 °C). Reference to Figure 3.7 indicates that both the CaO/CaS and MnO/MnS systems meet the above criteria for the realization of the desired extent of desulfurization. However, for the system MnO/MnS, operation beyond the eutectic point of 1232 °C may not be possible, although Turkdogan and Olsson⁴ indicate that this system performed well even at temperatures as high as 1300 °C.

3.7 Example 2

The following example will illustrate the proposed procedure for coal gasification followed by product gas desulfurization with manganese oxide or a manganese-based sorbent. Consider a gasification process carried out at 1200 °C for the Illinois No. 6 coal at an equivalence ratio of 2.5. Figure 3.3 indicates that P_{O_2} is fixed at a value of approximately $10^{-13.2}$ atm. Figure 3.4 shows clearly that among Mn, MnO, and Mn_3O_4 , MnO is the stable phase under the specified thermodynamic conditions. Figure 3.5 shows that MnS is stable with respect to $MnSO_4$ formation. Since MnO is the stable desulfurizing agent (and not Mn), there is no need to examine Figure 3.6 and consider the Mn/MnS equilibrium as the desulfurization reaction. Instead, one should examine Figure 3.7 and the MnO/MnS equilibrium, for which the standard free energy may be read from the ordinate as 190 kJ per mol of S_2 . Figure 3.8 need not be considered in this specific case because of the above-discussed relative instability of the sulfate. Based upon Figure 3.9 and the value of the free energy change for the desulfurization reaction deemed appropriate at the given temperature, one can estimate the ratio of P_{S_2}/P_{O_2} to be approximately 10^7 . Since P_{O_2} is known, one can calculate P_{S_2} as $10^{-6.2}$ atm. Knowing P_{S_2} and P_{O_2} values one may now examine Figures 3.12a and 3.12b to estimate the percentage of sulfur removal and H_2S concentration (ppm), respectively. These values are approximately 91.1% sulfur removal and 489.5 ppm H_2S .

3.8 Summary

The figures presented in this analysis enable an operator of a slagging combustor or coal gasifier, operating on a specific coal, to determine the equivalence ratio and temperature required for a given set of sorbents. This analysis is readily changed by use of the computer programs stated for any coal composition. Similar figures can be generated for another coal composition which would enable new desulfurization conditions to be evaluated. (However for the present examples, since results are presented in terms of percent sulfur removal, they will not be significantly different so long as the coal rank remains similar to the chosen Illinois No. 6 coal.) Extension of this approach to mixed-metal systems (e. g. zinc ferrite) requires input of the data for such a system into the database.

3.9 References

1. Hepworth, M. T.; Reid, K. J. Slagging Combustor Review. Final Report

- MRRRC, University of Minnesota, December, 1990.
2. Grindley, T.; Steinfeld, G. Testing of Zinc Ferrite Hydrogen Sulfide Absorbent in a Coal Gasifier Sidestream. *Proceedings of the Fourth Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas streams*; Markel, K.E., Ed.; U.S. Government Printing Office; DOE/METC-85/3(DE85001954); Dec 1984; pp 314-336.
 3. Jha, M. C.; Hepworth, M. T. Enhanced Sorbent Durability for Hot Gas Desulfurization; DOE Contract DE-AC21-84MC21168, Final Report, 1986.
 4. Turkdogan, E. T.; Olsson, R. G. Desulfurization of Hot Reducing Gases with Manganese Oxide Pellets. *Proceedings of the Third Iron and Steel Congress ASM*; ASM International: Materials Park, OH, 1979; pp 277-288.
 5. Hepworth, M. T.; Zhong, S. Thermodynamic Comparison of Lime as a Desulfurizer with Iron in Coal Combustion Atmospheres: Fe-FeO-Liquid Equilibrium. *Energy Fuels* 1991, 5, 237-243.
 6. Westmoreland, P. R.; Harrison, D. P. Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases. *Environ. Sci. Technol.* 1976, 10, 659-661.
 7. Westmoreland, P. R.; Gibson, J. B.; Harrison, D. P. Comparative Kinetics of High-Temperature Reaction Between H₂S and Selected Metal Oxides. *Environ. Sci. Technol.* 1977, 11, 488-491.
 8. Morris, A. E.; Flynn, H.; Carter, D. *Using the UMR STEPSOL Package; Version 4.0*; Generic Mineral Technology Center for Pyrometallurgy, University of Missouri at Rolla: Rolla, MO, 1990.
 9. Eriksson, G. *Chem. Scr.* 1975, 8, 100-103.
 10. Eriksson, G.; Bjorkman, B. *Can. Metall. Q.* 1982, 21, 329-337.
 11. Eriksson, G.; Rosen, E. *Scan. J. Metall.* 1973, 2, 95-99.
 12. Eriksson, G.; Johansson, T. *Scan. J. Metall.* 1978, 7, 264-270.
 13. Johansson, T.; Eriksson, G. *Scan. J. Metall.* 1980, 9, 283-291.
 14. Thompson, W. T.; Pelton, A. D.; Bale, C. W. *FACT Guide to Operations*, 1985.
 15. Turnbull, A. G.; Wadsley, M. W. *The CSIRO-SGTE THERMODATA System*, Program CHEMIX User's Guide.
 16. Flynn, H.; Morris, A. E.; Carter, D. An Iterative Gas-Phase Removal Version of SOLGASMIX. *Proceedings of the 25th CIM Conference of Metallurgists, TMS-CIM*, Toronto, Ontario, 1986.
 17. Pelton, A. D.; Bale, C. W. *Metall. Trans. A* 1986, 17A, 1211-1215.
 18. Morris, A. E.; Ben-Slimane, R.; Mang, W. Phase Equilibria and Thermodynamic Modelling of the Lead-Sulfur-Oxygen System and Applications to Direct Lead Smelting. *Mervyn Willis Symposium and Smelting & Refining Course*, 6-8 July, 1992; Nilmani, M., Rankin, W. J., Eds.; University of Melbourne: Melbourne, Australia; pp 8:1-8:14.
 19. Rao, Y. K. *Stoichiometry and Thermodynamics of Metallurgical Processes*; Cambridge University Press: Cambridge, U.K., 1985, pp 790-818.
 20. *North American Combustion Handbook*, 2nd ed.; Reed, R. J., Ed.; North

- American Mfg. Co.: Cleveland, Ohio, 1978.
21. Barin, I.; Knacke, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances, Supplement*, 1977.
 22. Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag: New York, 1973.
 23. Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry*, 5th ed.; Pergamon Press: New York.
 24. Turkdogan, E. T. *Physical Chemistry of High Temperature Technology*; Academic Press: New York, 1980.
 25. *Bull.--U.S. Bur. Mines* 1984, 677.
 26. *JANAF Thermochemical Tables*, 3rd ed.; American Chemical Society and American Institute of Physics, 1985.
 27. Hepworth, M. T.; Wicker, G. R. Iron Oxide as a Desulfurizing Agent in a Slagging Coal Combustor. *Pyrometallurgy '87*; Institution of Mining and Metallurgy: London, 1987.

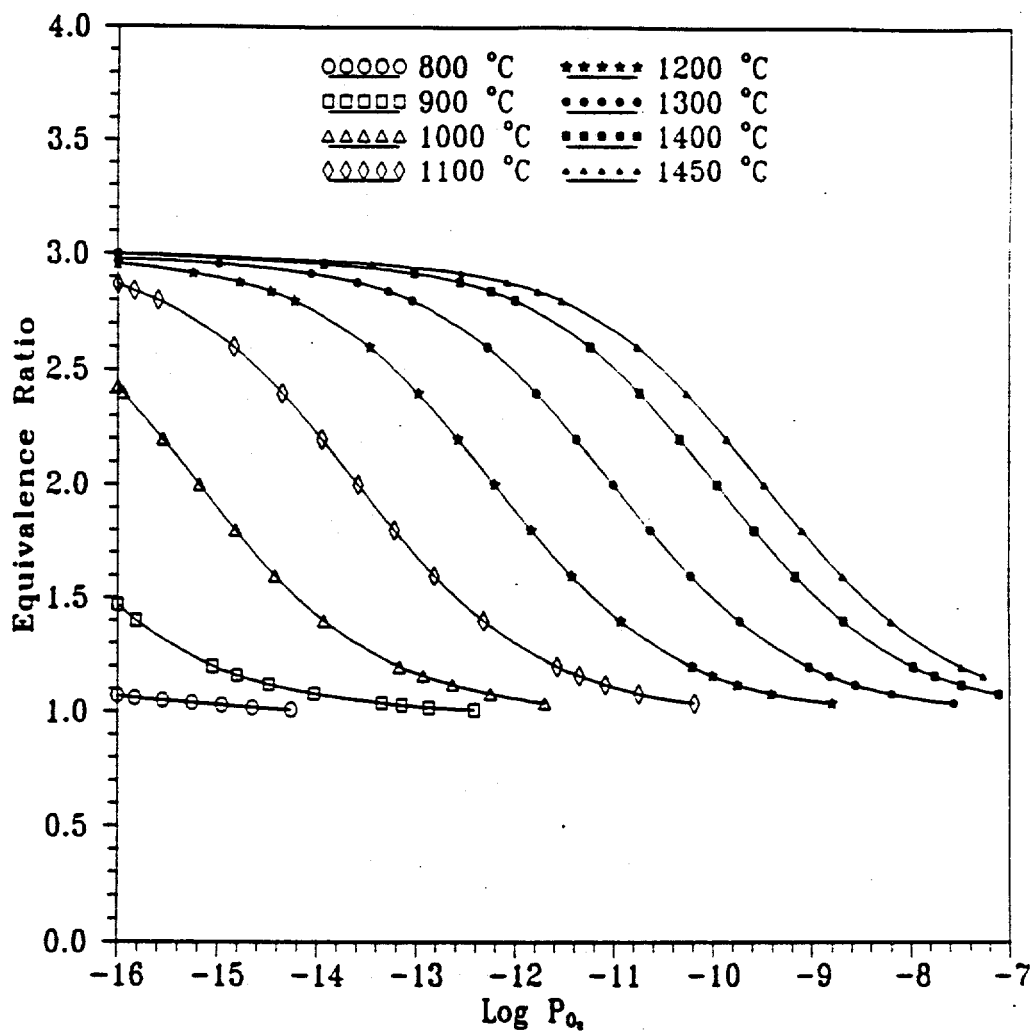


Figure 3.1 Equivalence ratio vs oxygen partial pressure (atmosphere) at several temperatures for an Illinois No. 6 coal.

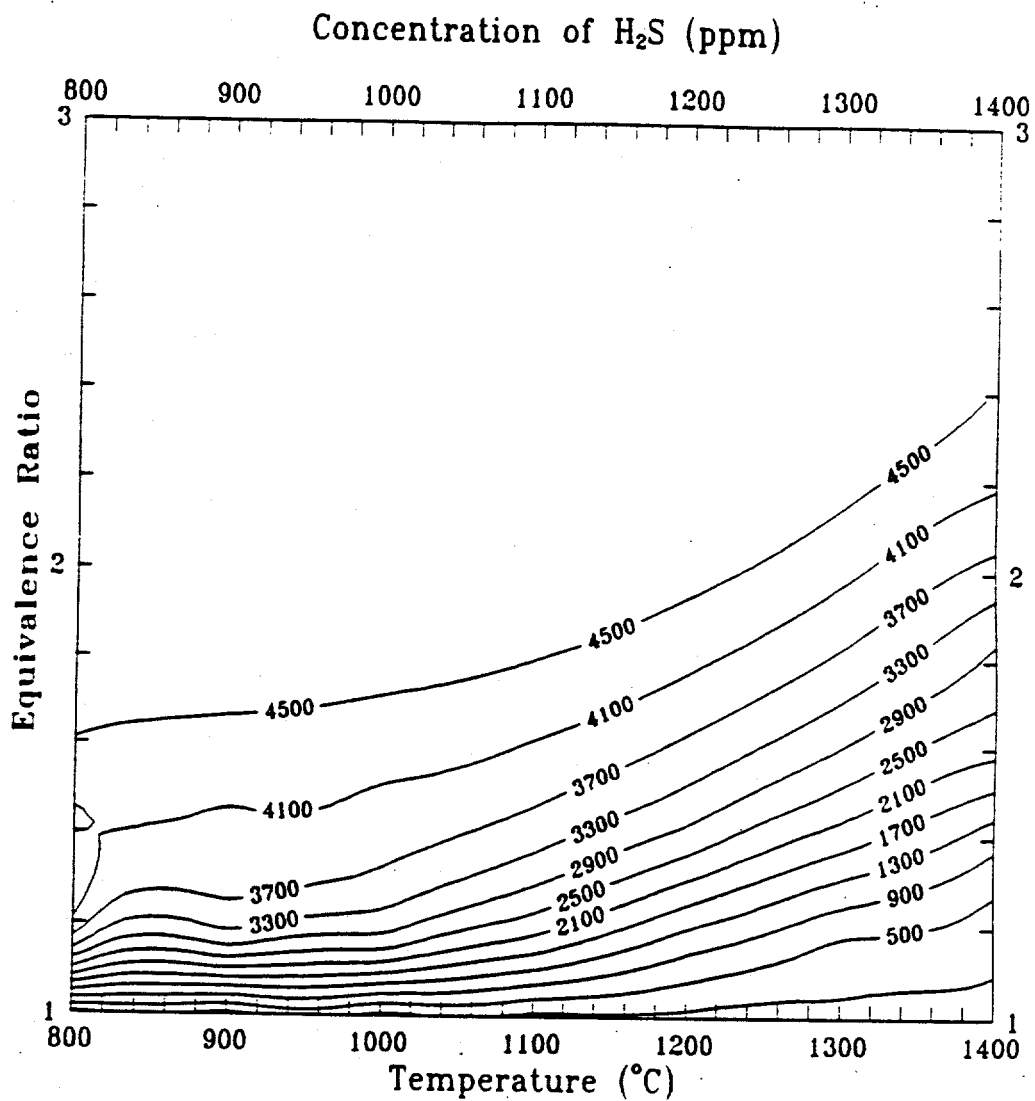


Figure 3.2a Concentration of H₂S (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

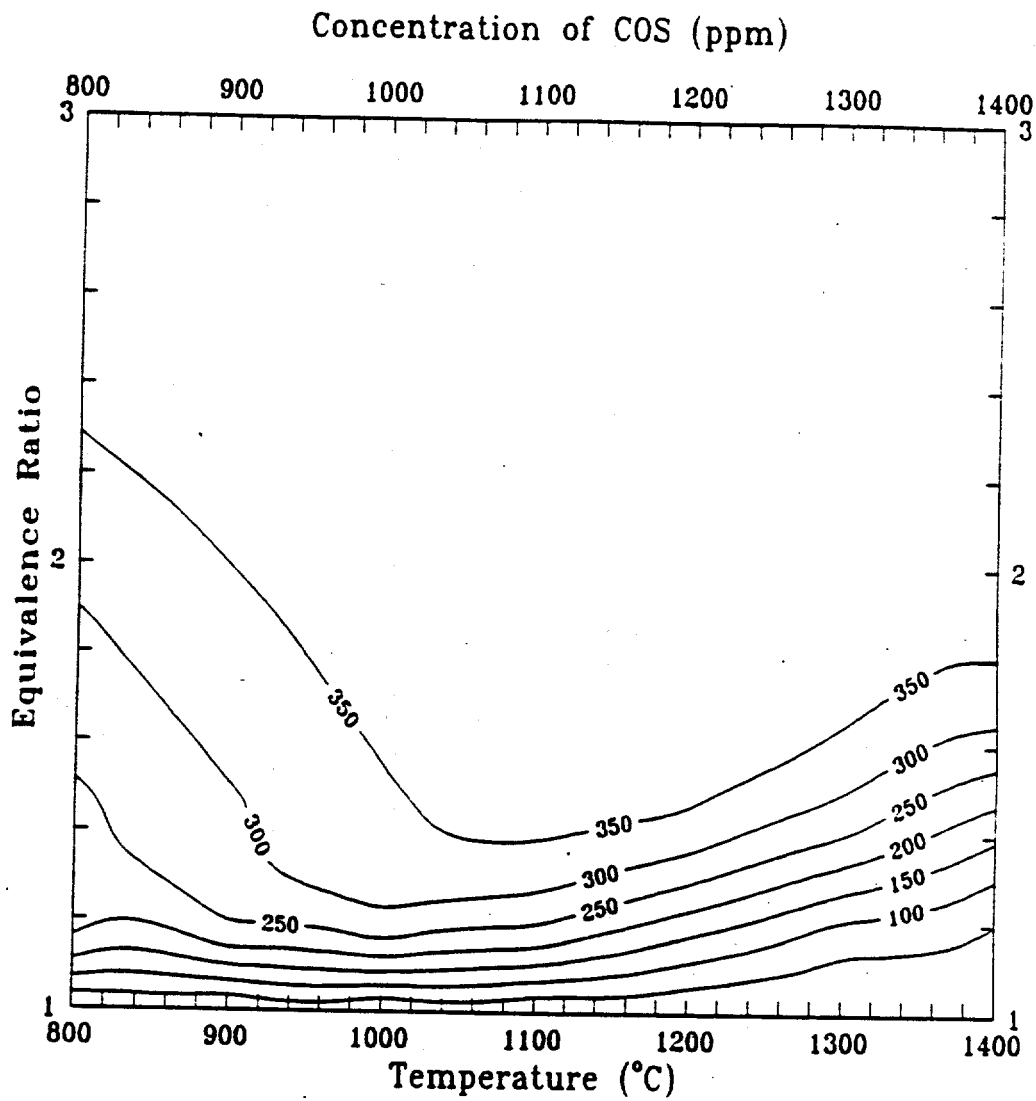


Figure 3.2b Concentration of COS (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

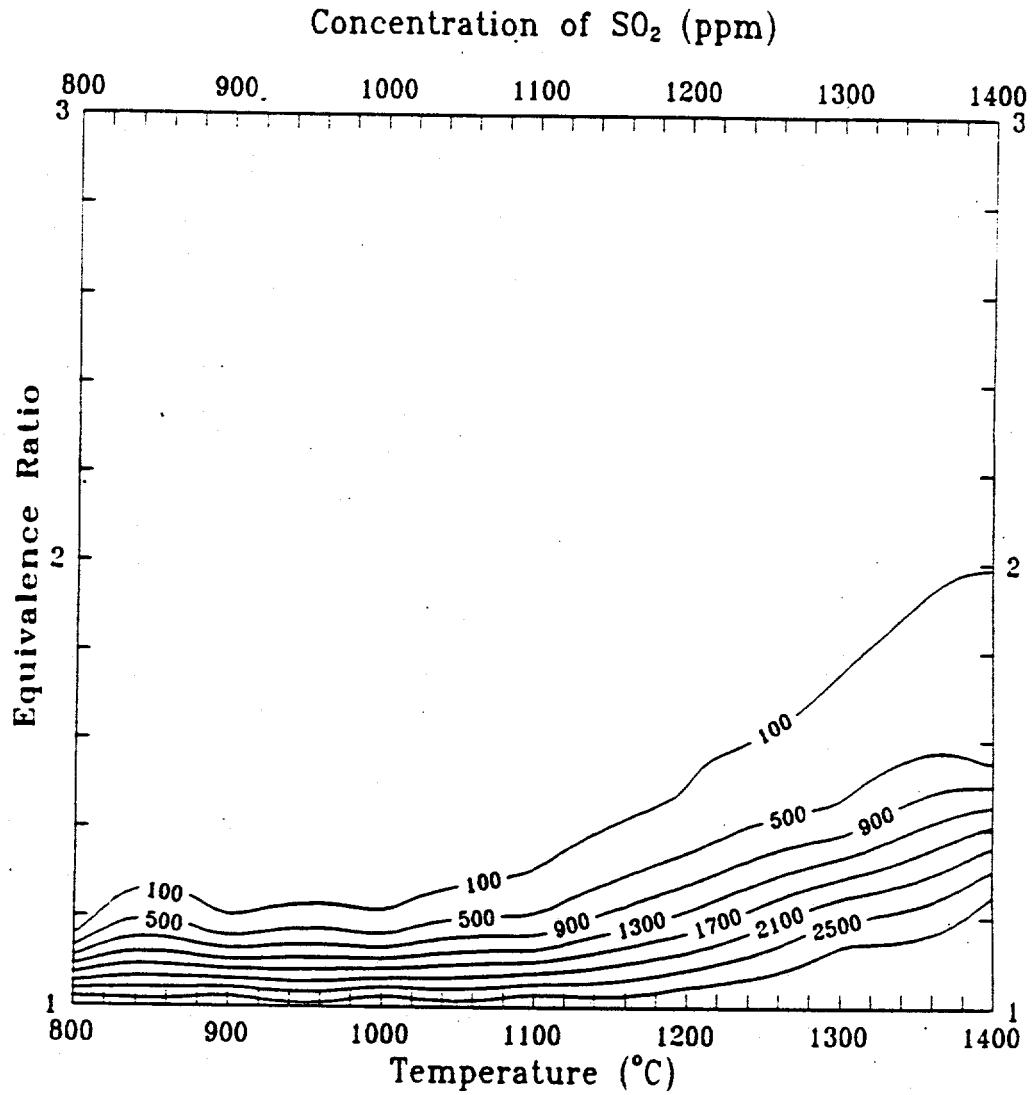


Figure 3.2c Concentration of SO₂ (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

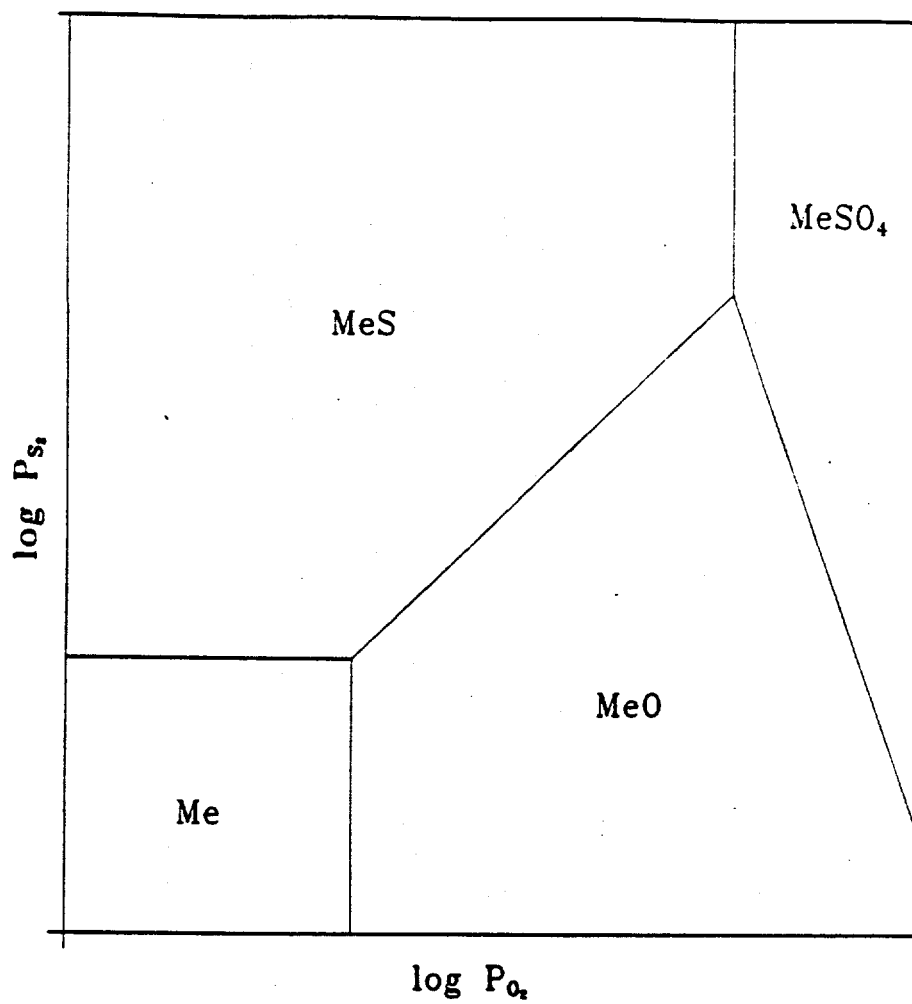


Figure 3.3 Stability diagram for a hypothetical divalent metal-sulfur-oxygen (M-S-O) system at a fixed temperature.

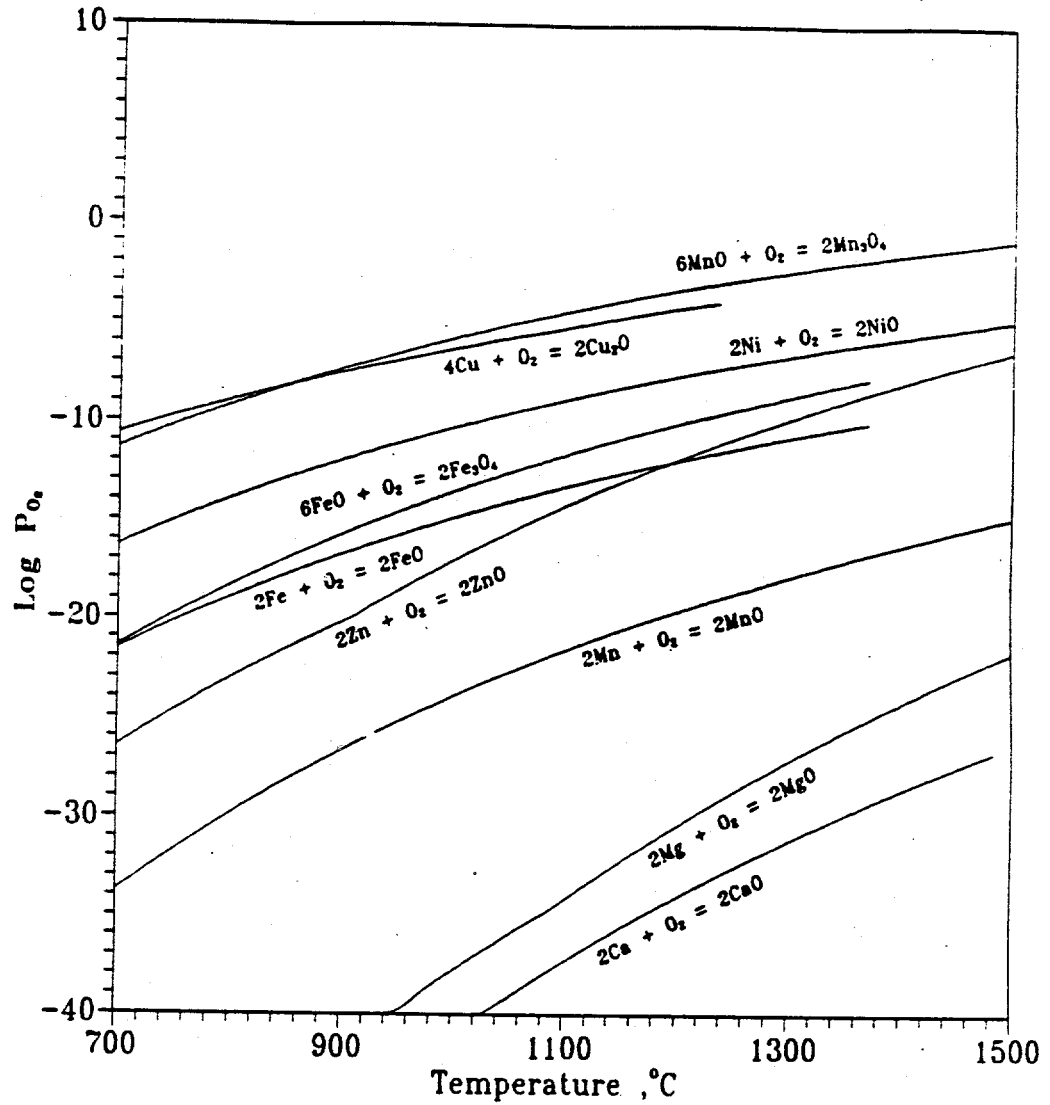


Figure 3.4 Stability of several metal/metal oxide combinations as a function of oxygen partial pressure (atmosphere) and temperature ($^{\circ}\text{C}$).

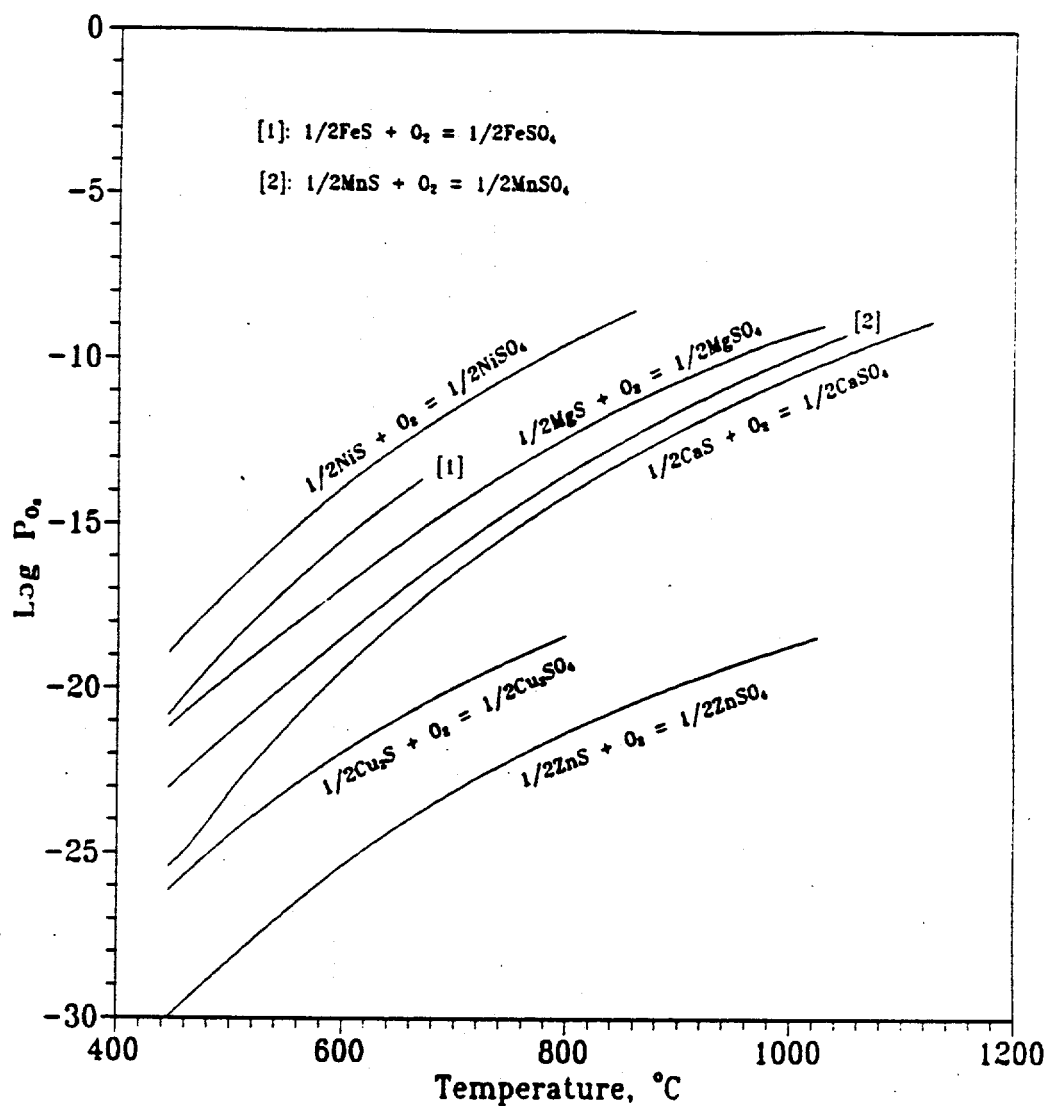


Figure 3.5 Stability of several metal sulfide /metal sulfate combinations as a function of oxygen partial pressure (atmosphere) and temperature (°C).

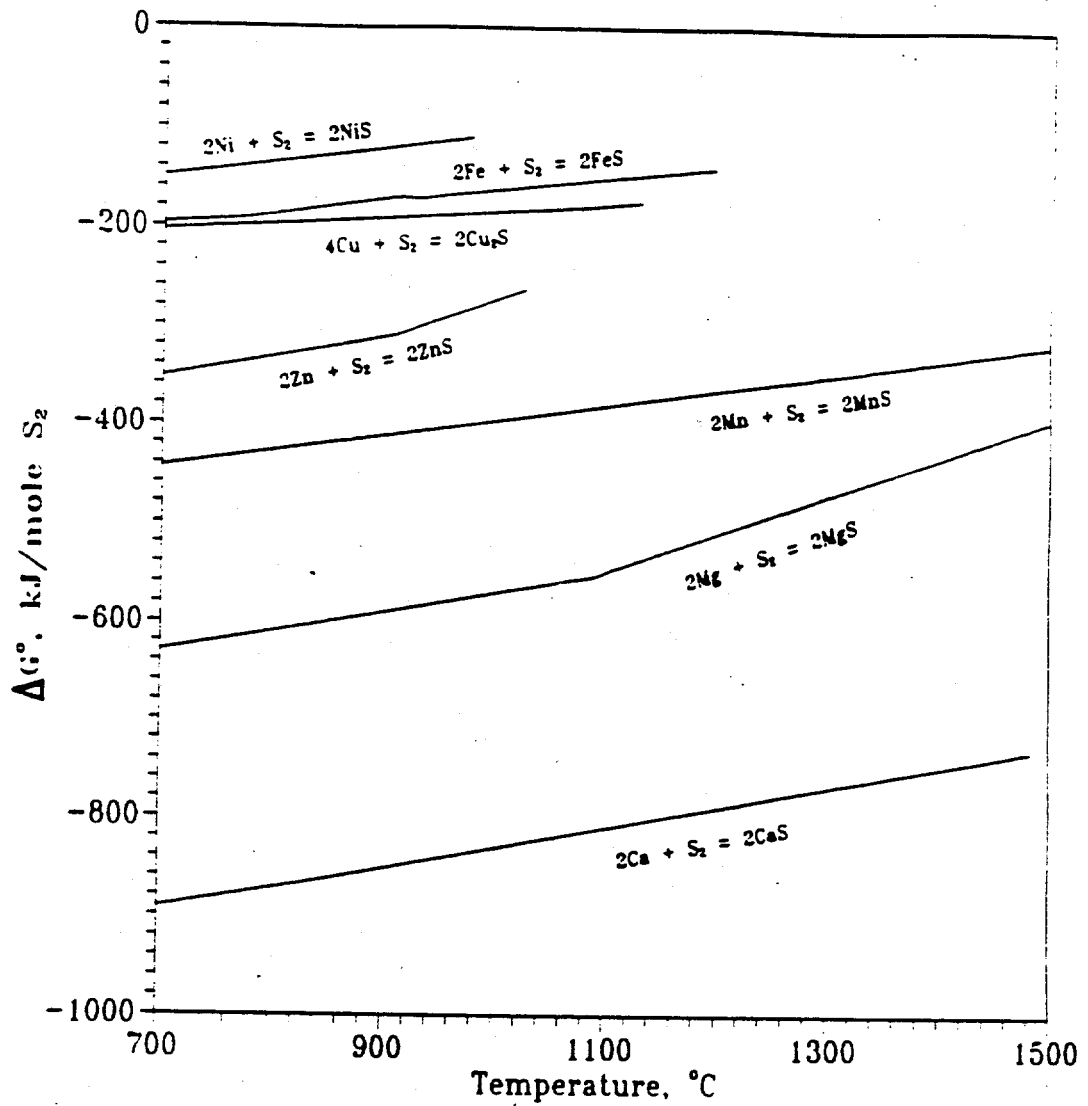


Figure 3.6 Free energy (in kJ/mol S_2) vs temperature ($^\circ C$) stability diagram for several metal/metal sulfide combinations.

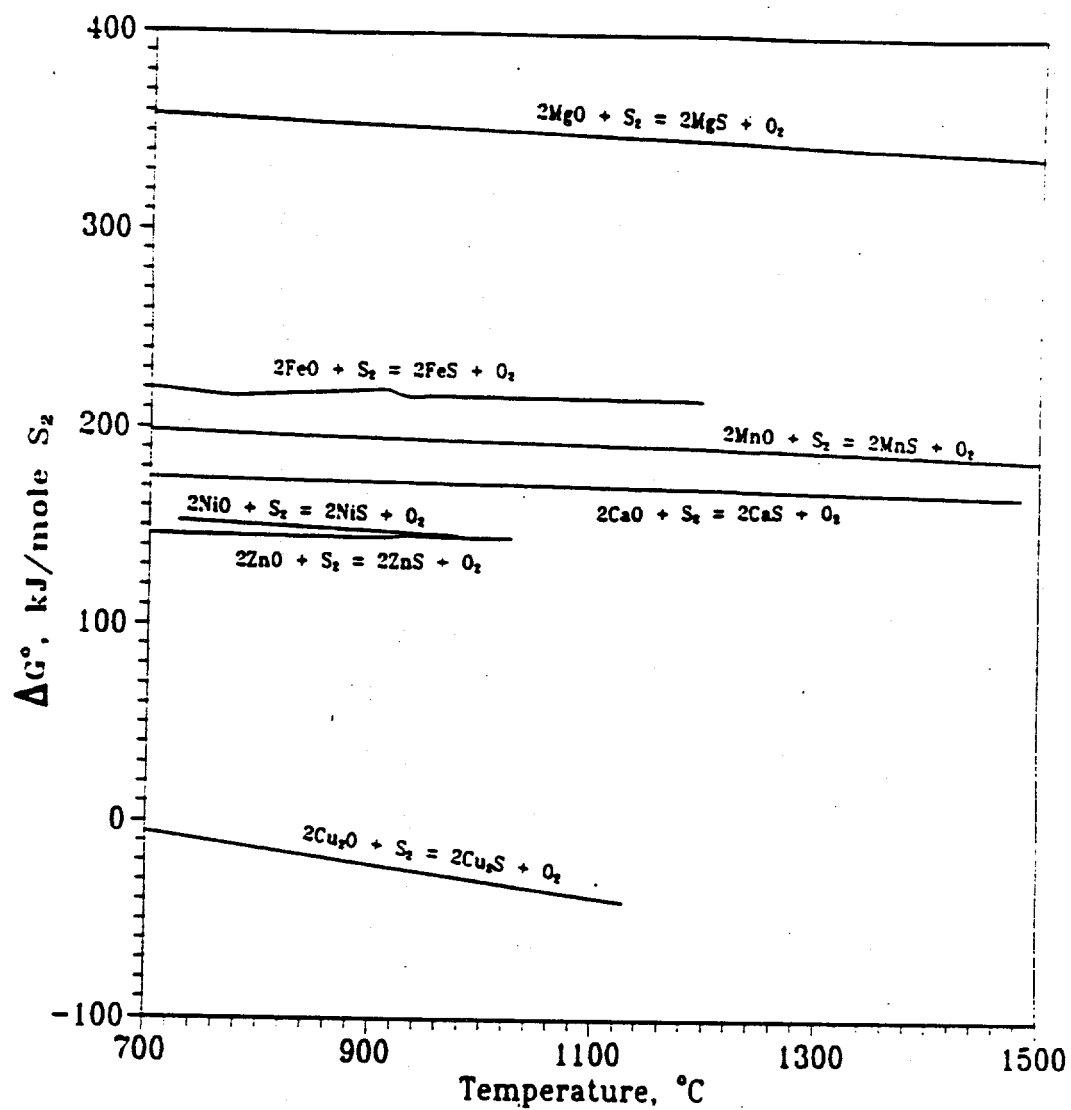


Figure 3.7 Free energy (in kJ/mol S_2) vs temperature ($^\circ C$) stability diagram for several metal oxide/metal sulfide single-metal systems.

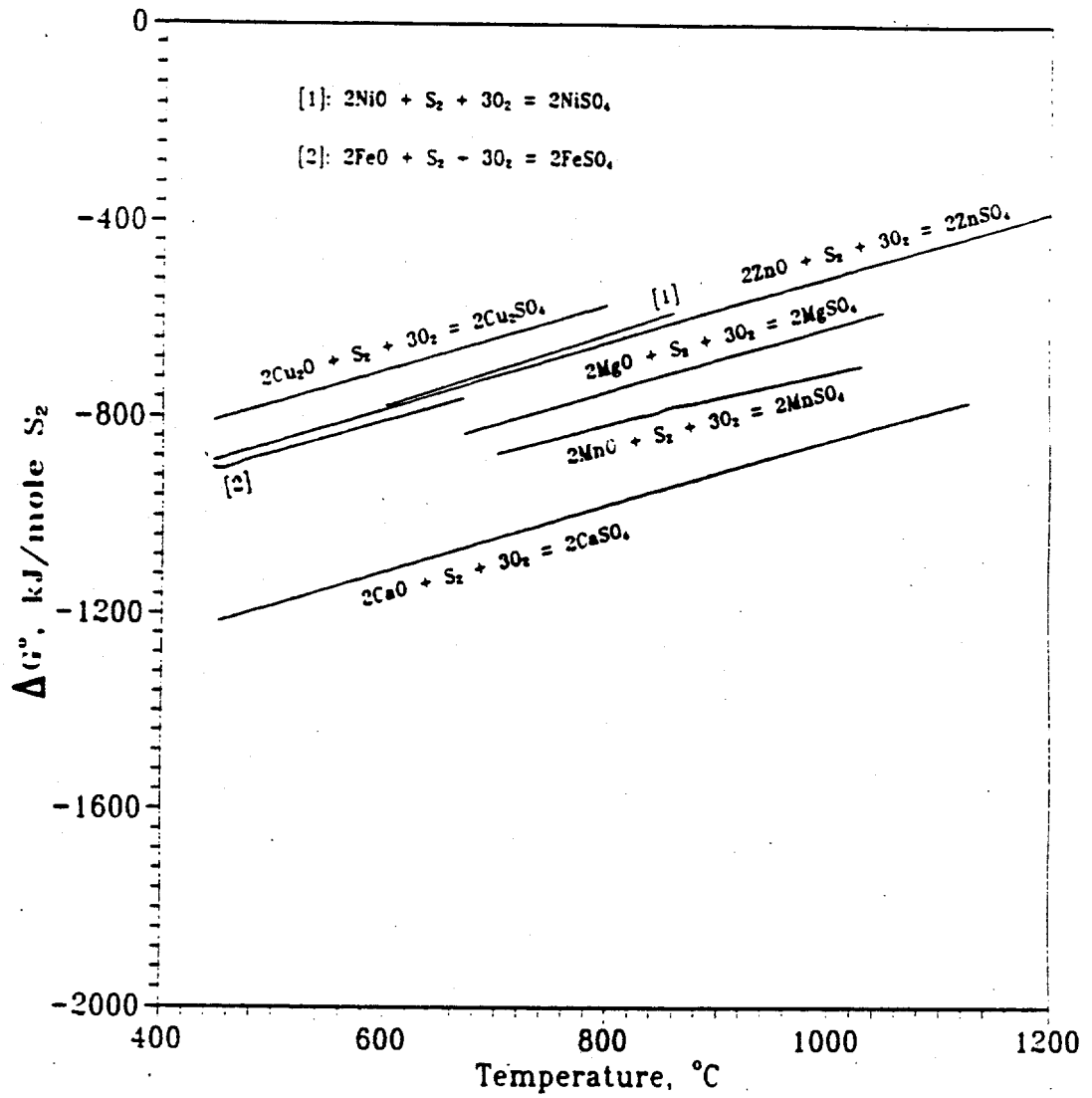


Figure 3.8 Free energy (in kJ/mol S_2) vs temperature ($^\circ C$) stability diagram for several metal oxide/metal sulfate systems.

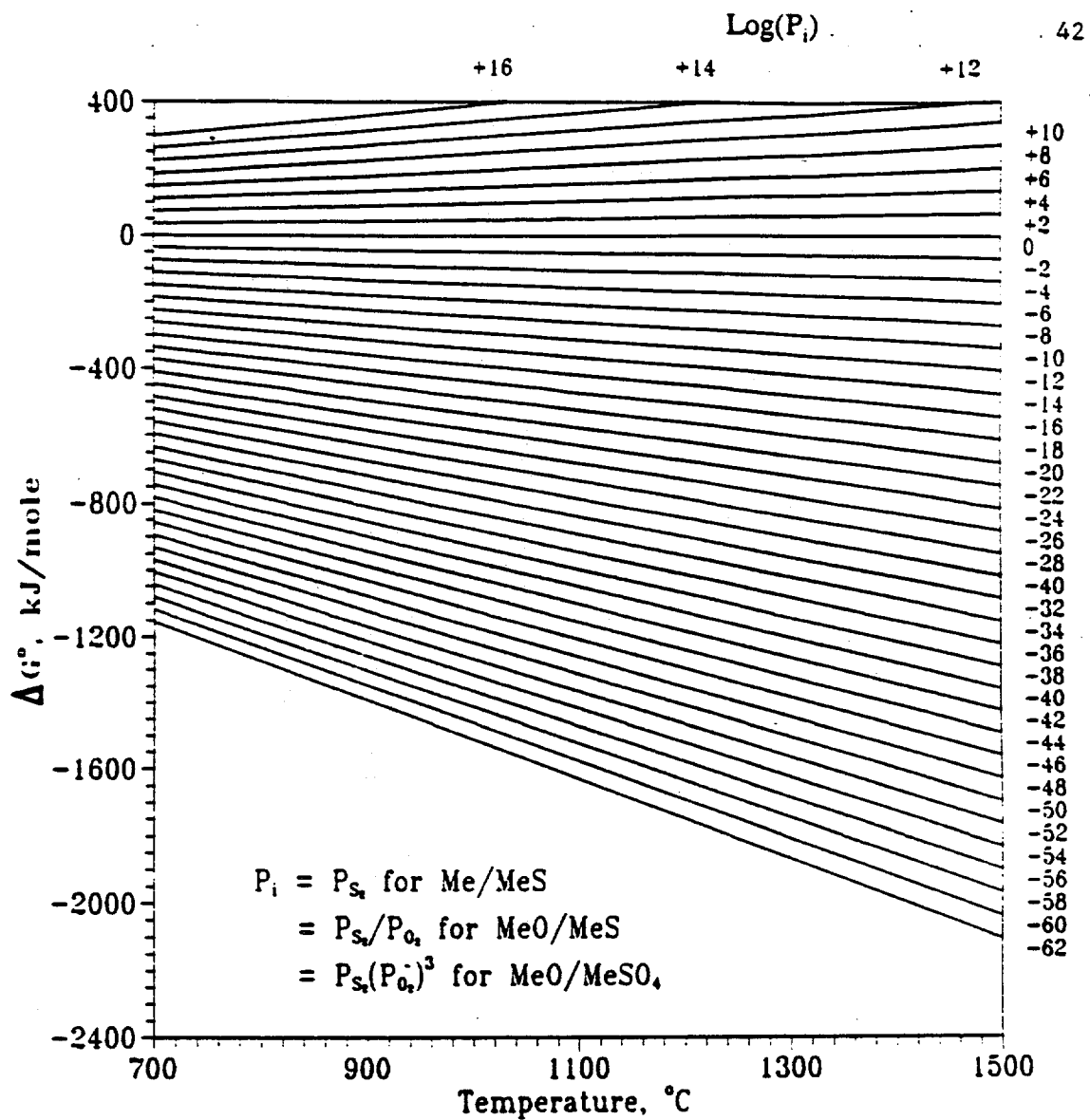


Figure 3.9 Composite representation of free energy (in kJ/mol) vs temperature (°C) stability diagram for metal/metal sulfide, metal oxide/metal sulfide, and metal oxide/metal sulfate systems.

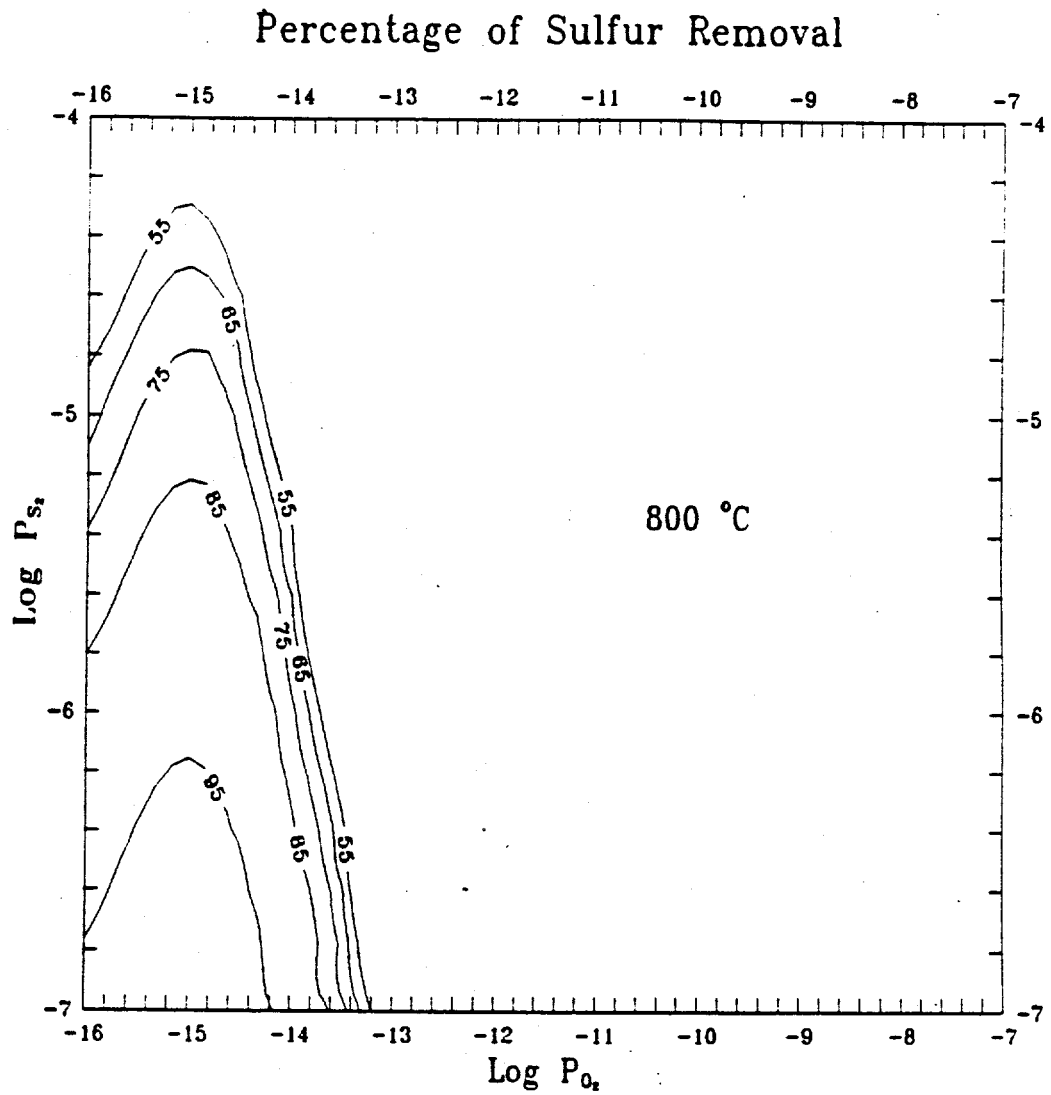


Figure 3.10a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 800 °C (Illinois No. 6 coal).

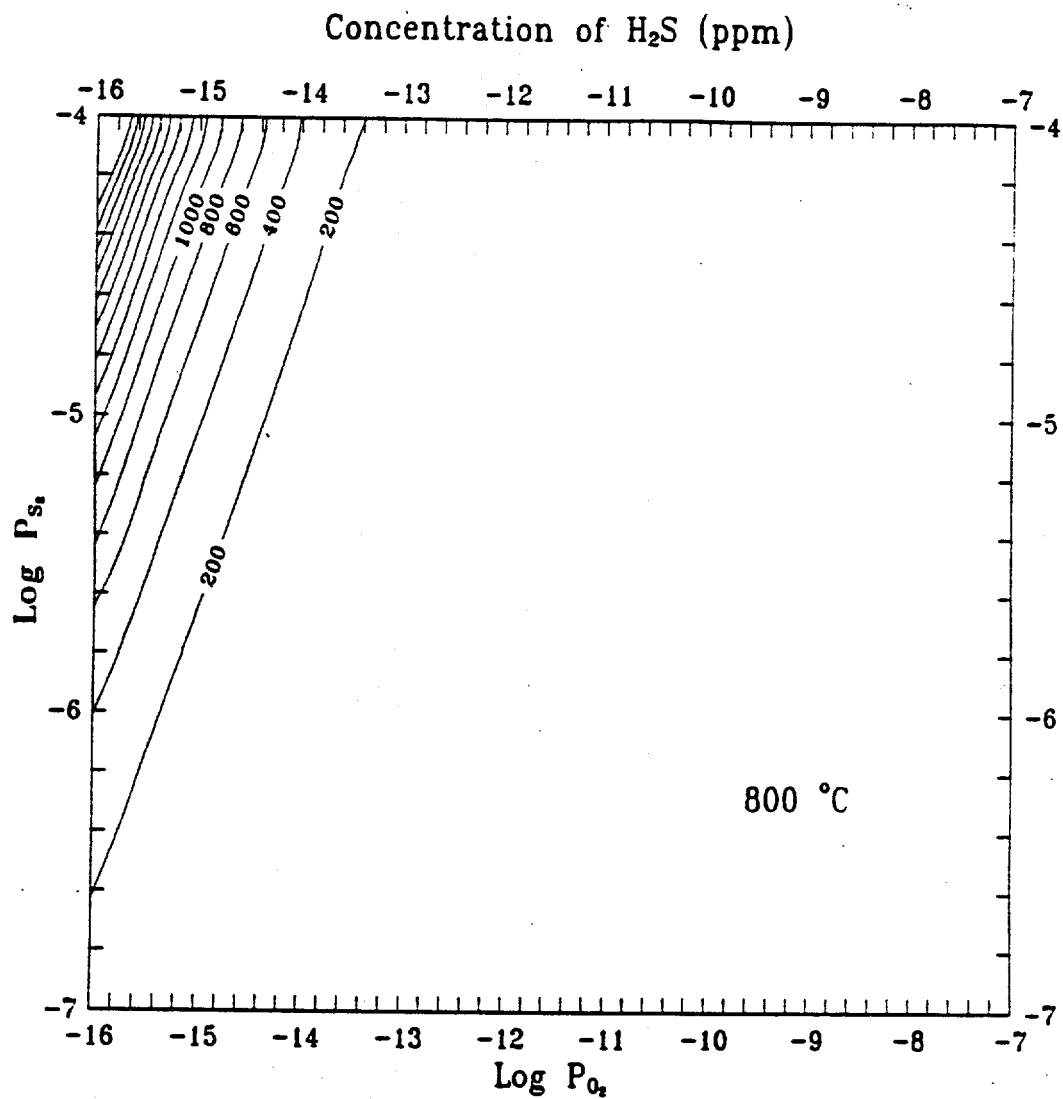


Figure 3.10b Concentration of H₂S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 800 °C (Illinois No. 6 coal).

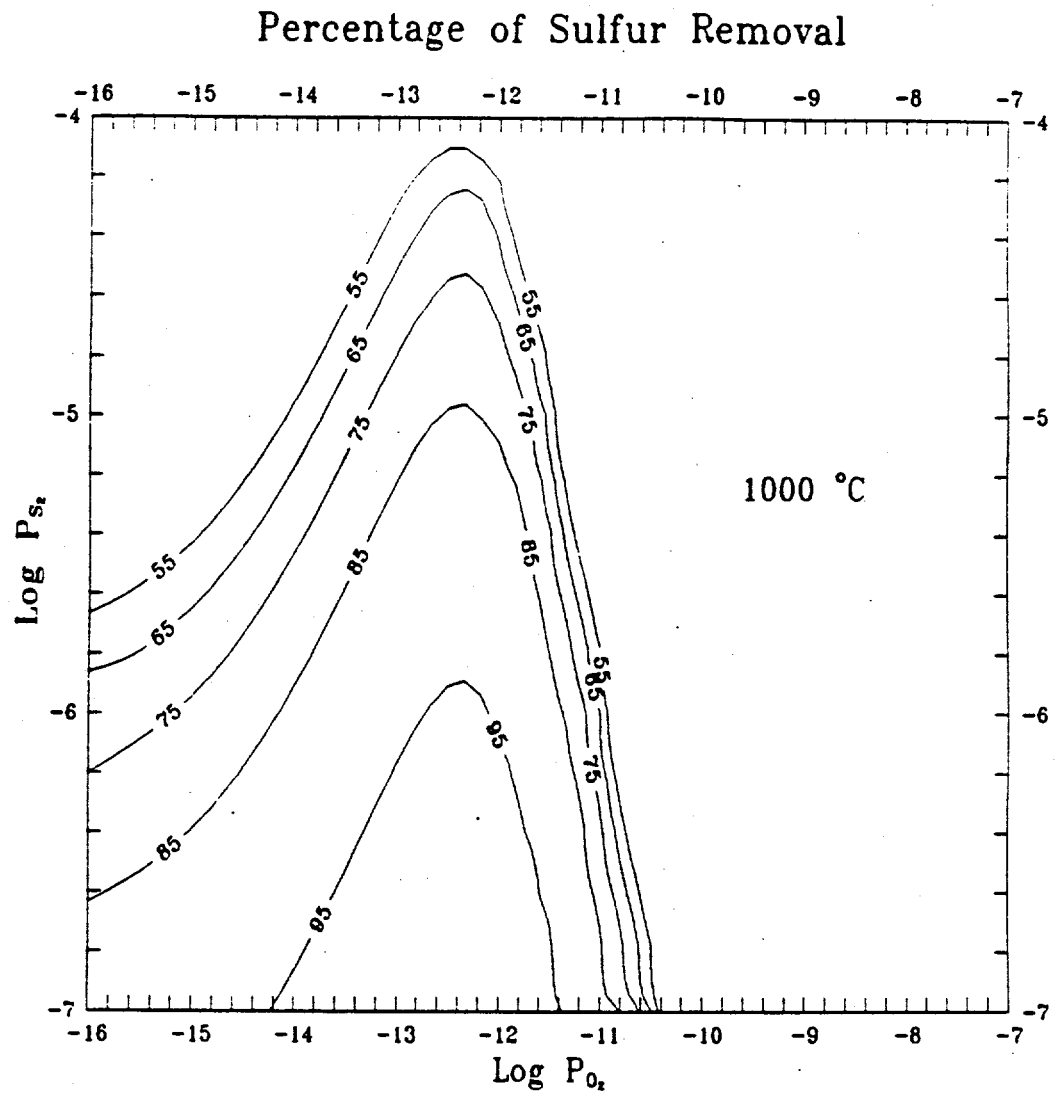


Figure 3.11a Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1000 °C (Illinois No. 6 coal).

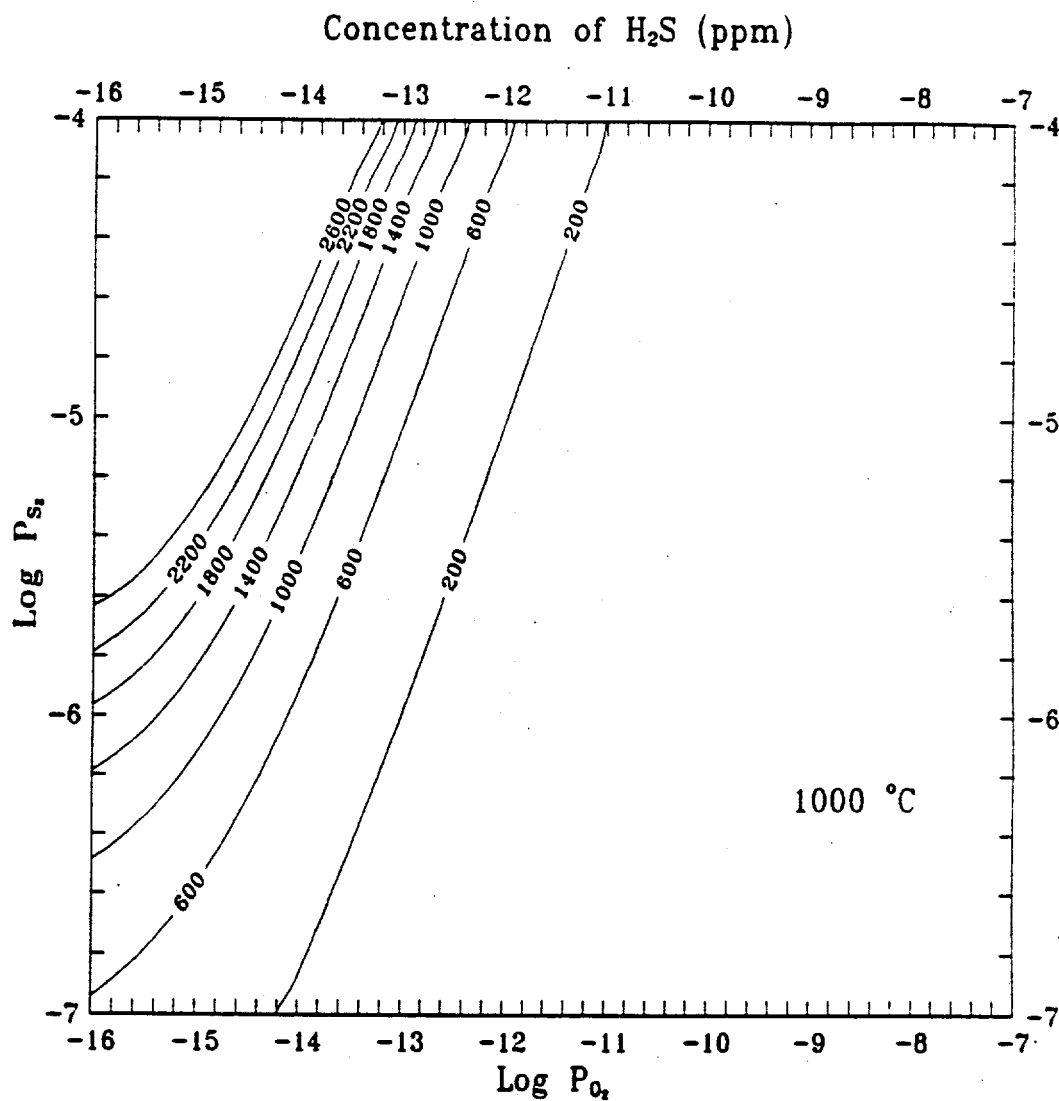


Figure 3.11b

Concentration of H₂S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1000 °C (Illinois No. 6 coal).

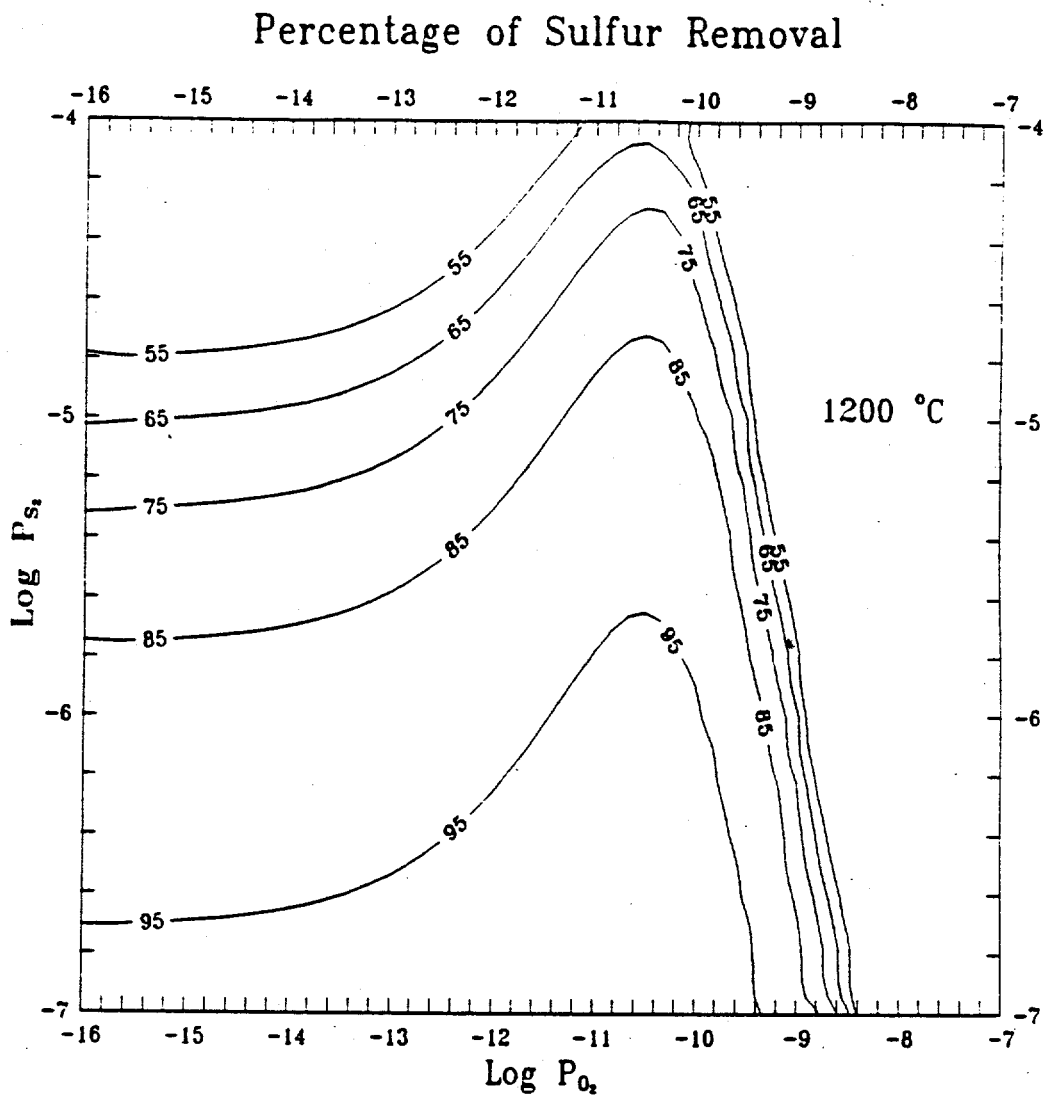


Figure 3.12a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at $1200\text{ }^\circ\text{C}$ (Illinois No. 6 coal).

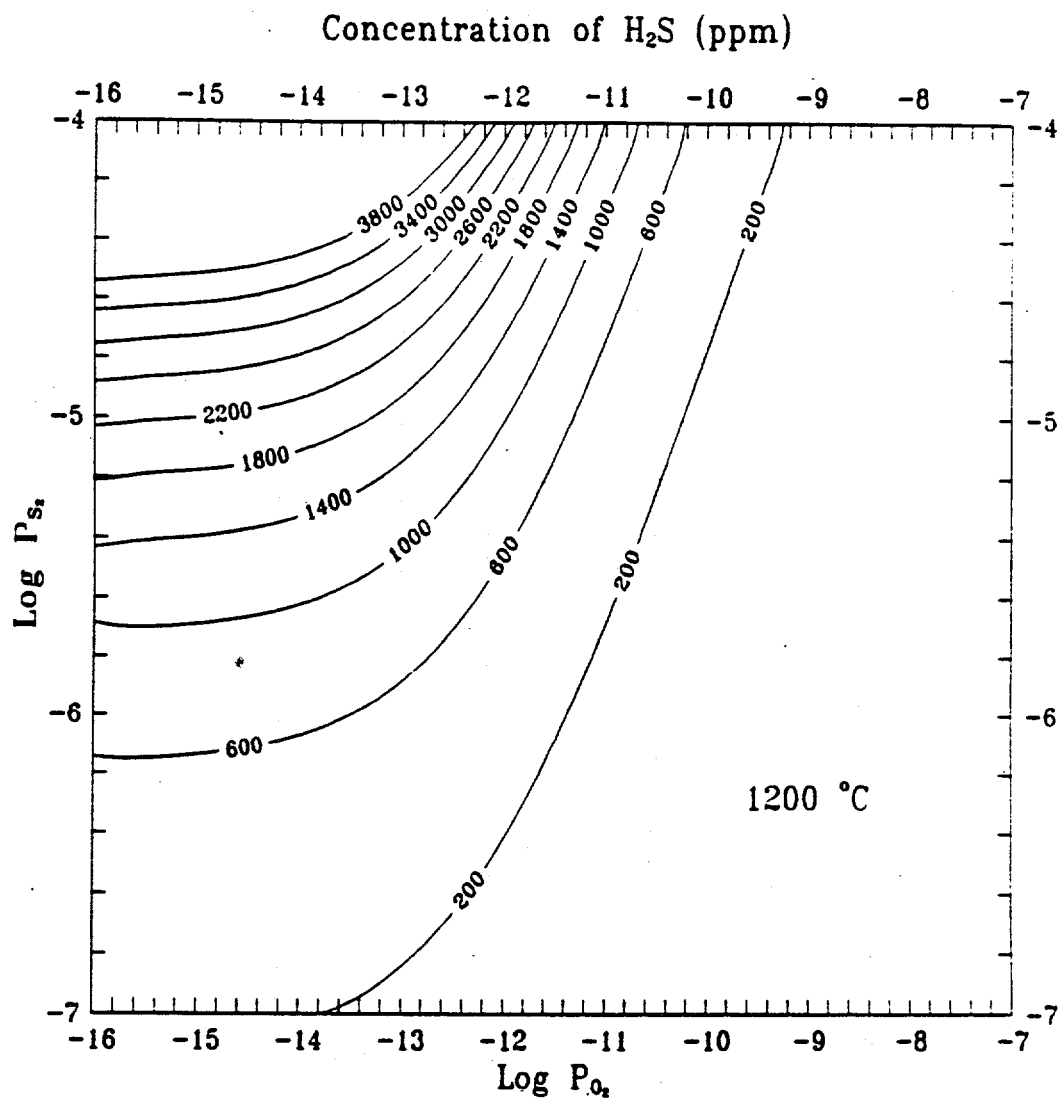


Figure 3.12b

Concentration of H_2S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1200 °C (Illinois No. 6 coal).

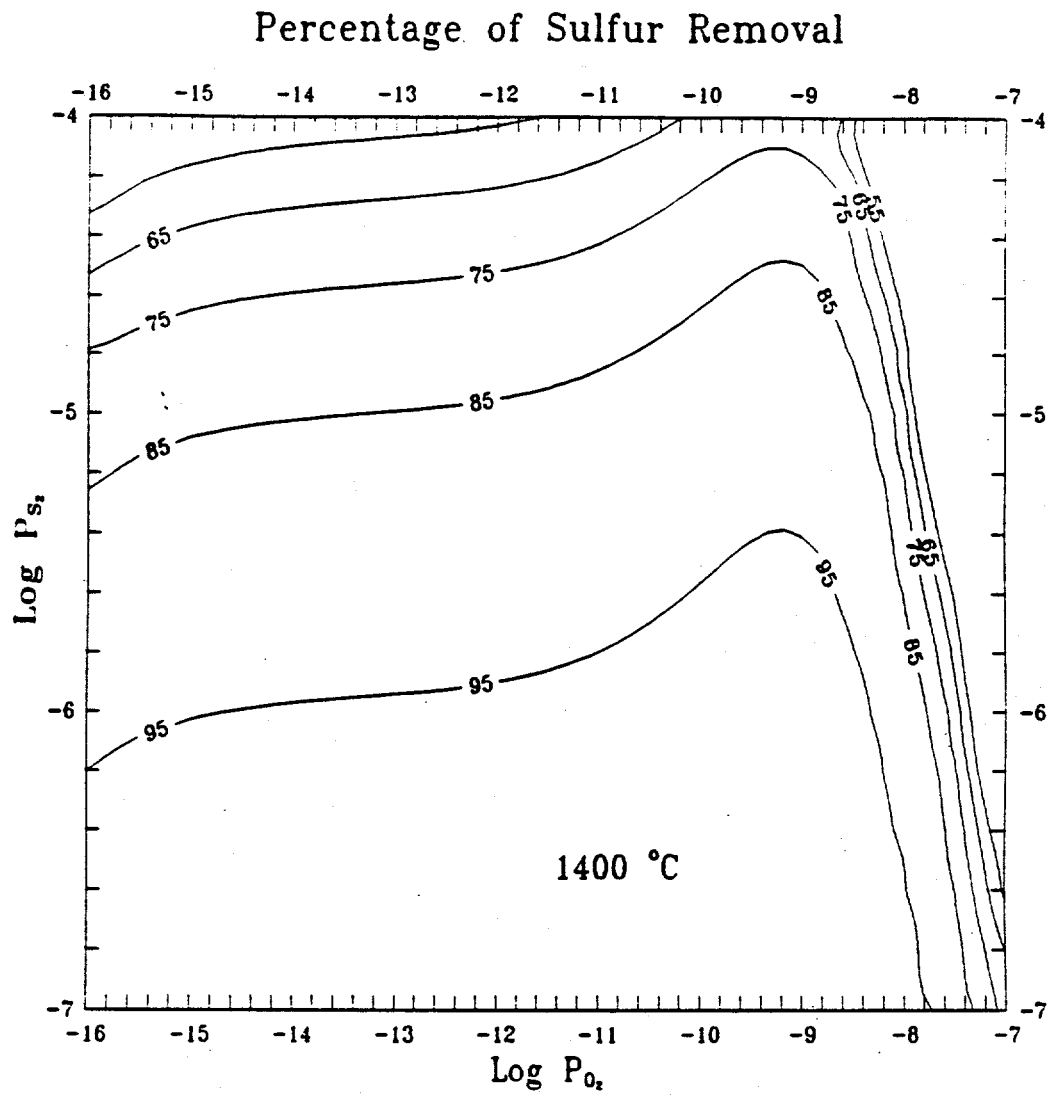


Figure 3.13a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1400 °C (Illinois No. 6 coal).

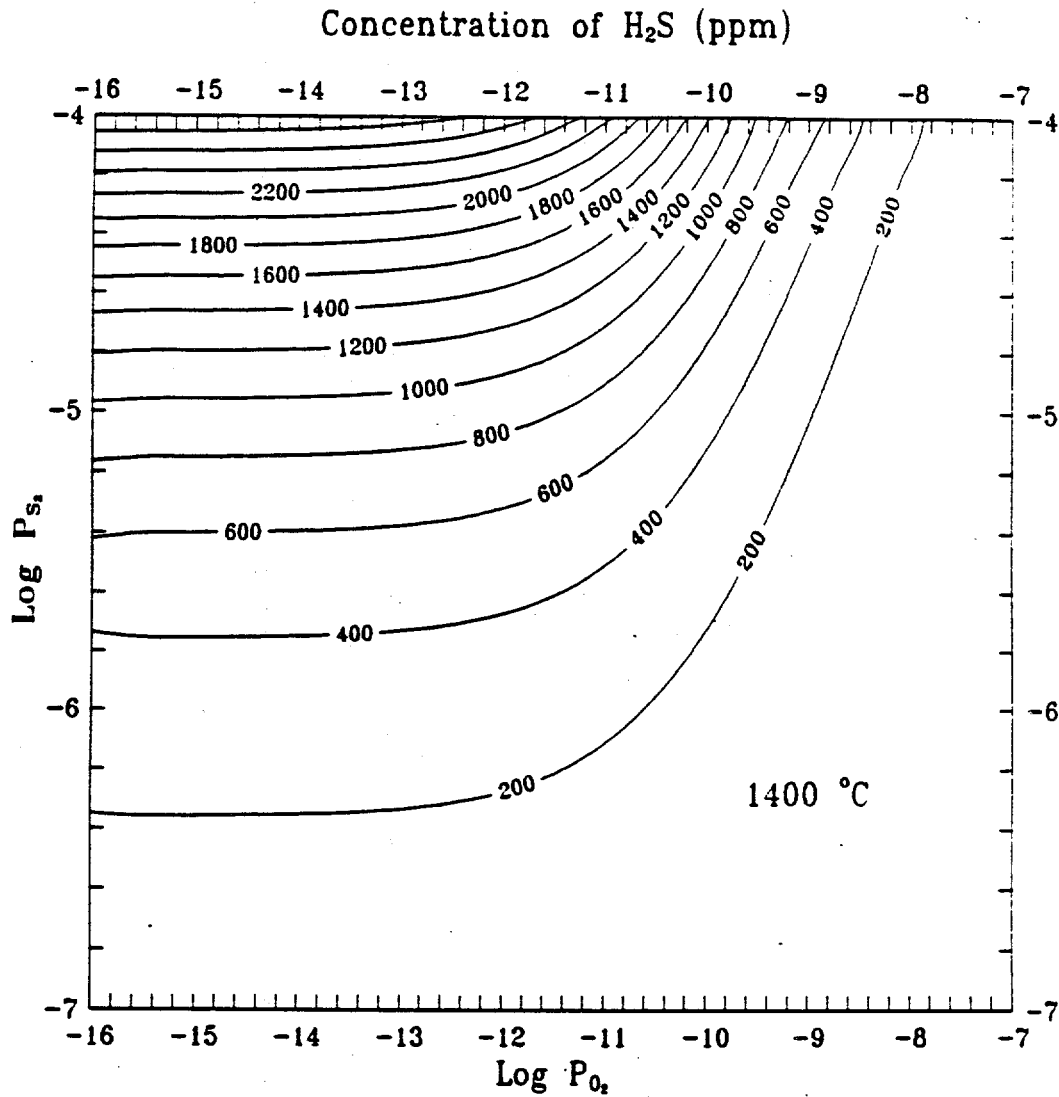


Figure 3.13b

Concentration of H₂S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1400 °C (Illinois No. 6 coal).