



Industrial uses of high sulfur petroleum coke
by Lance Harold Ulrich

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

The purpose of this thesis is to find a use or uses for high sulfur petroleum coke. Research was conducted to determine if high sulfur petroleum coke can be used as a reagent to convert molybdenum ore, MoS_2 , to MoO_2 . The second experiment was to determine if the petroleum coke can be used as a reagent to convert Cu_2S ore to copper at a lower temperature than is currently used in industry. The third area of research was to determine if high sulfur petroleum coke could be used in place of regular coke to reduce iron ore, Fe_3O_4 , to pig-iron (Fe). The last experiment was to determine if petroleum coke could be substituted for regular coke in the initial lead ore roasting process.

Each of these experiments used a similar procedure. The petroleum coke was mixed with the metal ore, and the mixture was heated in either an oxidizing or reducing atmosphere until the ore had been converted to the final product. Then the product was chemically analyzed to determine purity and percent conversion. For molybdenum, the ore/coke mix was cooked in air to facilitate the conversion of MoS_2 to MoO_2 . Air was blown through an experimental blast furnace to help convert Cu_2S ore to elemental copper. A reducing atmosphere was required to convert iron ore, Fe_3O_4 , to iron, so the ore/coke mix was insulated from the atmosphere with a top layer of coke. Lastly, air was blown through the lead ore/coke mix to help convert PbS to Pb.

An 83% conversion of MoS_2 to MoO_2 was obtained by roasting an 8:1 coke:ore mixture in air at 500°C for 38 minutes. The iron ore didn't reduce to iron at 1350°C . The best result with copper ore was achieved by roasting a 0.5:1 coke:ore ratio at 700°C with a small amount of air blowing through it. After two hours a 60% conversion of Cu_2S to Cu was achieved. A 43% conversion of PbS to Pb was obtained by roasting a 0.167:1 coke:ore ratio in air for 8 minutes at 800°C .

It was concluded that it is highly probably that high sulfur petroleum coke is effective in converting MoS_2 to MoO_2 and it is highly probable that the petroleum coke can be used to convert lead ore to lead. The coke is effective in converting copper ore to copper. Lastly, high sulfur petroleum coke cannot convert Fe_3O_4 to iron at 1350°C ; a higher temperature is probably needed.

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APPROVAL

of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF NOMENCLATURE

| Symbol | Definition | Units |
|-------------------------------|--|-------------|
| ΔG_T° | Gibbs standard energy change of reaction at constant temperature T | kcal/mol |
| ΔH_T° | Standard enthalpy change of reaction at constant temperature T | kcal/mol |
| T | Temperature | K |
| ΔS_T° | Standard entropy change of reaction at constant temperature T | cal/(K*mol) |
| ΔC_p° | Standard heat capacity of reaction at constant pressure | cal/(K*mol) |
| v_i | Stoichiometric coefficient of each component in the reaction, i (+) for products, (-) for reactants | none |
| C_{pi}° | Standard heat capacity of each component in the reaction, i | cal/(K*mol) |
| R | Gas constant | cal/(mol*K) |
| K | Equilibrium constant | none |
| $H_{\text{prod}, 298}^\circ$ | Sum of the standard enthalpies of the products of reaction | kcal/mol |
| $H_{\text{react}, 298}^\circ$ | Sum of the standard enthalpies of the reactants in the reaction | kcal/mol |
| $S_{\text{prod}, 298}^\circ$ | Sum of the standard entropies of the products of reaction | cal/(K*mol) |
| $S_{\text{react}, 298}^\circ$ | Sum of the standard entropies of the reactants in the reaction | cal/(K*mol) |

ABSTRACT

The purpose of this thesis is to find a use or uses for high sulfur petroleum coke. Research was conducted to determine if high sulfur petroleum coke can be used as a reagent to convert molybdenum ore, MoS_2 , to MoO_2 . The second experiment was to determine if the petroleum coke can be used as a reagent to convert Cu_2S ore to copper at a lower temperature than is currently used in industry. The third area of research was to determine if high sulfur petroleum coke could be used in place of regular coke to reduce iron ore, Fe_3O_4 , to pig-iron (Fe). The last experiment was to determine if petroleum coke could be substituted for regular coke in the initial lead ore roasting process.

Each of these experiments used a similar procedure. The petroleum coke was mixed with the metal ore, and the mixture was heated in either an oxidizing or reducing atmosphere until the ore had been converted to the final product. Then the product was chemically analyzed to determine purity and percent conversion. For molybdenum, the ore/coke mix was cooked in air to facilitate the conversion of MoS_2 to MoO_2 . Air was blown through an experimental blast furnace to help convert Cu_2S ore to elemental copper. A reducing atmosphere was required to convert iron ore, Fe_3O_4 , to iron, so the ore/coke mix was insulated from the atmosphere with a top layer of coke. Lastly, air was blown through the lead ore/coke mix to help convert PbS to Pb .

An 83% conversion of MoS_2 to MoO_2 was obtained by roasting an 8:1 coke:ore mixture in air at 500°C for 38 minutes. The iron ore didn't reduce to iron at 1350°C . The best result with copper ore was achieved by roasting a 0.5:1 coke:ore ratio at 700°C with a small amount of air blowing through it. After two hours a 60% conversion of Cu_2S to Cu was achieved. A 43% conversion of PbS to Pb was obtained by roasting a 0.167:1 coke:ore ratio in air for 8 minutes at 800°C .

It was concluded that it is highly probably that high sulfur petroleum coke is effective in converting MoS_2 to MoO_2 and it is highly probable that the petroleum coke can be used to convert lead ore to lead. The coke is effective in converting copper ore to copper. Lastly, high sulfur petroleum coke cannot convert Fe_3O_4 to iron at 1350°C ; a higher temperature is probably needed.

BACKGROUNDPetroleum Coke

Heavy oils that are left over after vacuum distillation in a refinery are worth very little since they can only be used as fuel. However, light oils can be further processed to make saleable products. Lighter oils can be produced from very heavy ones solely by thermal cracking. This process is called "coking" because the by-product is petroleum coke.

The feed to a coker is usually the heavy gas oil that is left over from vacuum distillation of the lubricating residue. The lubricating residue comes from crude oil distillation. The coker produces either delayed coke or fluid coke. Delayed coke is available in chunks while fluid coke is in the form of small spherical balls. In either case, the chemical composition of the coke is 93 - 99% carbon and the balance is sulfur. [1]

Both delayed and fluid coke are valuable as electrolytic reducing agents if their sulfur content is below 3%. In the refining of sulfur containing crude oil, the pitch, asphalt and coke fractions contain the most sulfur. If the crude is a high sulfur crude, the coke fraction can become 5 - 7% sulfur. After coking, most of the sulfur in this fraction ends up in the petroleum coke. Currently, high sulfur petroleum coke is

almost worthless. Even as a fuel, the current restriction is one pound of sulfur per million BTU's. [2]

The EXXON refinery in Billings, Montana uses a high sulfur crude as its feedstock. The petroleum coke produced by this refinery is about 94% carbon and 6% sulfur so it cannot be used as an electrolytic reducing agent or as a fuel. The research in this thesis is based upon trying to find a use for the high sulfur petroleum coke produced at the EXXON Refinery in Billings. [3] The properties of the EXXON fluid coke are presented in Table 1. Properties of EXXON Fluid Petroleum Coke.

Table 1. Properties of EXXON Fluid Petroleum Coke [4]

Sieve Analysis

| <u>Cumulative, % Retained</u> | | <u>Non-cumulative, % Retained</u> | |
|---|-------------------|-----------------------------------|---------------------|
| <u>on:</u> | 10m --- 2 | <u>on:</u> | 12m --- 4.2 |
| | 20 --- 5 | | 20 --- 3.9 |
| | 48 --- 11 | | 40 --- 6.4 |
| | 60 --- 20 | | 50 --- 37.6 |
| | 80 --- 44 | | 70 --- 29.2 |
| | 100 --- 65 | | 100 --- 10.0 |
| | 150 --- 88 | | 200 --- 6.4 |
| | 200 --- 95 | | 325 --- 1.2 |
| | Through 200 --- 5 | | Through 325 --- 1.1 |
| <u>Particle Density, g/cm³</u> | | 1.3 | |
| <u>Bulk Density, lb/ft³</u> | | 55.9 | |
| <u>Calorific Value, BTU/lb</u> (ASTM D-271) | | 14,100 | |
| <u>Proximate Analysis, wt. %</u> (ASTM D-271) | | | |
| Moisture | | 0.3 | |
| Volatile Matter | | 6.0 | |
| Fixed Carbon | | 93.4 | |
| Ash | | 0.3 | |
| <u>Ultimate Analysis, wt. %</u> (ASTM D-271) | | | |
| Carbon | | 90.0 | |
| Hydrogen | | 2.0 | |
| Sulfur | | 6.0 | |
| <u>Metals, (wt. % on coke)</u> | | | |
| Nickel | | 0.013 | |
| Vanadium | | 0.034 | |
| Iron | | less than 0.01 | |
| Calcium | | less than 0.01 | |
| Silicon | | less than 0.005 | |
| Titanium | | less than 0.001 | |
| Sodium | | less than 0.02 | |

Molybdenum

Molybdenum was discovered in 1778 by C. W. Scheele when he produced a new oxide from molybdenite (MoS_2), thus distinguishing the mineral from graphite, with which it had been thought to be identical. Today, molybdenum is obtained from molybdenite and is a byproduct from the production of copper. In both cases, MoS_2 is separated by floatation and then roasted in air to produce MoO_3 . About 85% of the MoO_3 is used in the manufacture of stainless steel and high-speed tools. It is used directly or after conversion to ferromolybdenum by the aluminothermic process.

Molybdenum chemicals are synthesized from ammonium molybdate which is obtained by dissolving MoO_3 in aqueous ammonia, then crystallizing the ammonium molybdate. Pure molybdenum, which is used in catalysts for a variety of petrochemical processes and as an electrode material, is obtained from hydrogen reduction of ammonium molybdate. [5]

The intent of the molybdenum research is to determine if molybdenum ore, MoS_2 , can be converted to MoO_2 using high sulfur petroleum coke as a reagent, thus demonstrating a use for the coke. MoO_2 is of interest because it contains 11% more molybdenum per pound than MoO_3 .

Several investigators have reported methods of converting

molybdenite to MoO_2 :

"V. H. Zazhigalov (1975) employed hydrogen and elemental sulfur. N. Satani (1975) used hydrogen-thiophene mixtures to reduce the MoO_3 hydrate to MoO_2 . J. O. Besenhard (1976) carried out the reduction of MoS_2 in dimethylsulfoxide. A. Wold (1964) prepared pure MoO_2 crystals by the electrolytic reduction of MoO_3 -- NaMoO_4 solution. W. Kunzman (1961) used a mixture of CO and CO_2 to reduce MoO_3 to MoO_2 . S.I. Sobol (1961) used hydrogen and CO under pressure at 200°C . to reduce NaMoO_4 to MoO_2 . V. Angelova (1972) reacted molybdenite with TiO_2 at 500° -- 900°C to produce MoO_2 , SO_2 and elemental Ti. F. Zabo (1963) reduced MoO_3 with ammonia." [6]

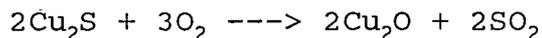
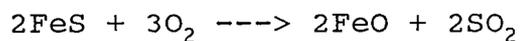
Additional work on the subject includes Conversion of Molybdenite to Molybdenum Dioxide Using Petroleum or Coal Tar Pitches. This patent states that "Molybdenite, MoS_2 , is completely converted into molybdenum dioxide, MoO_2 by mixing MoS_2 with petroleum or coal tar pitches and heating in air at 400° - 600°F ." [7]

Copper

Copper is one of the most important metals in the history of man. It was in use as far back as 5000 BC, was obtained from charcoal reduction in 3500 BC, and was combined with tin to establish the "Bronze Age" in about 3000 BC. Today, copper is still one of man's most important metals.

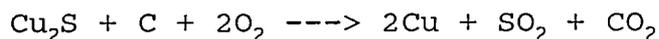
The majority of copper comes from huge open pit mines. The ore only contains about 1/2% Cu so it is concentrated to 15-20% Cu by froth floatation before further processing.

Silica is added to the concentrate, and the mixture is melted in a reverberatory furnace at about 1400°C. The iron in the melt (FeS) is more readily converted to the oxide than the Cu₂S ore, so it forms an upper layer of iron silicate slag. This leaves a lower layer of copper matte which is mostly Cu₂S and FeS. The liquid matte is poured into a converter, more silica is added, and a blast of air is forced through it. The air and silica transforms the remaining FeS to FeO and then to slag, while the Cu₂S is converted to Cu₂O and then to copper:



This "blister" copper is usually further purified electrolytically for use in the electronics industry. [8]

The research in this thesis involves using petroleum coke as a reagent to convert Cu₂S ore to Cu at a lower temperature. If this is proven, it will demonstrate a use for the high sulfur petroleum coke. The probable reaction is as follows:



This reaction represents the overall conversion of Cu₂S to Cu. There is probably an intermediate step where the copper is in an oxidized state, but this is not important because the above equation is only used to obtain a rough approximation of temperatures at which Cu₂S can be converted to Cu.

Iron

As with copper, iron has had a tremendous impact on man's history. Iron beads dating from about 4000 BC were probably of meteoric origin. Iron was first made by low temperature reduction methods, but this produces a spongy material that could only be shaped by prolonged hammering. The high temperature smelting process did not evolve until about 1200 BC--the start of the "Iron Age". More recently, the use of coke as the reducing agent had far-reaching effects, such as the start of the Industrial Revolution.

Today, most iron is used as steel of one form or another. The first step to convert iron ore to steel is the blast furnace. The Fe_2O_3 ore is reduced to Fe using coke as the reducing agent while limestone (CaCO_3) removes sand or clay as slag (see Figure 1, Iron Blast Furnace). The molten iron is cast into molds or ingots for further processing. This iron is in an impure form containing about 4% carbon and is called "cast-iron" or "pig-iron". [9]

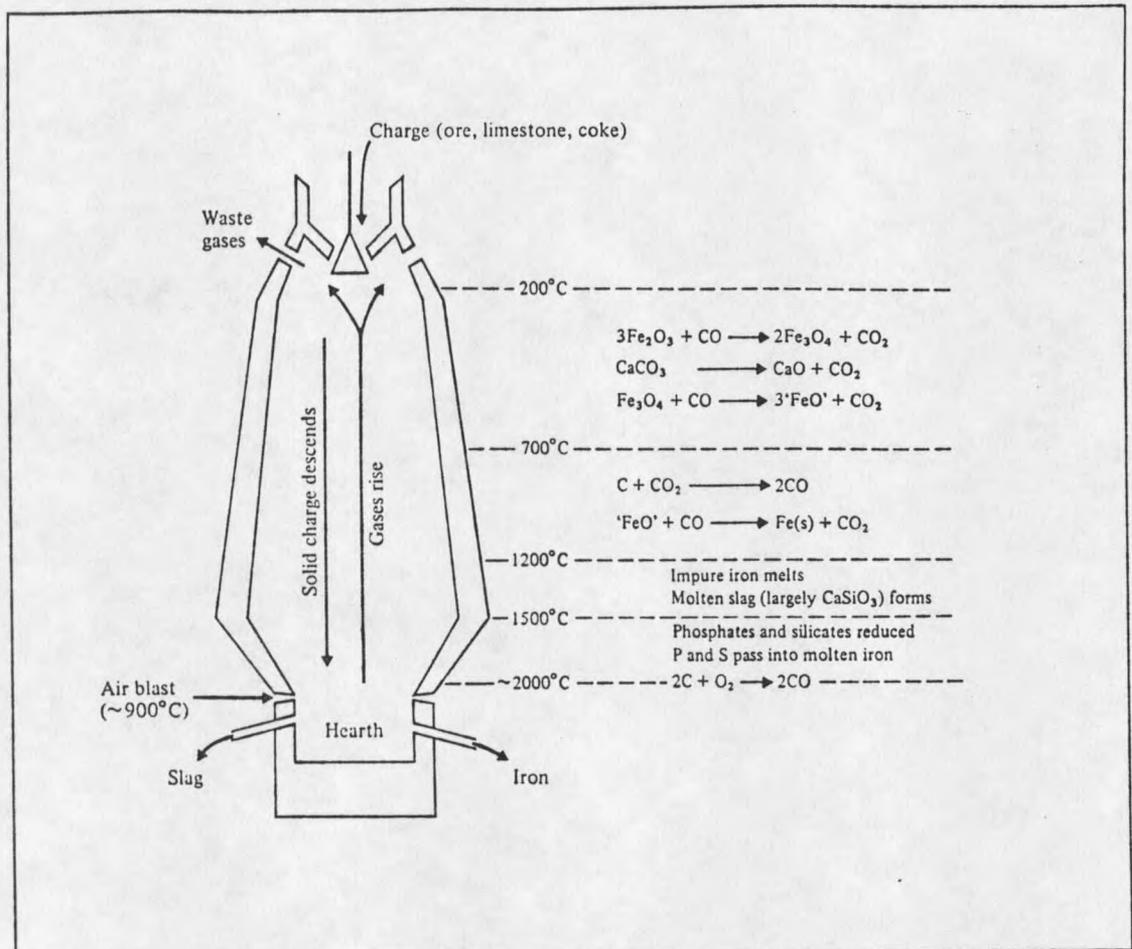


Figure 1, Iron Blast Furnace

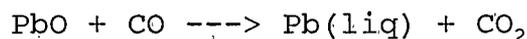
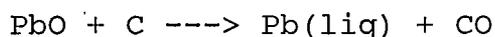
The purpose for this research on iron is to find out if petroleum coke could be used in place of regular coke to reduce the iron ore to pig-iron.

Lead

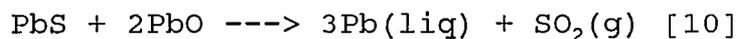
Lead is another of man's oldest metals. It was used in ancient Egypt for glazing pottery in 7000-5000 BC. The Romans

used lead for water pipes and plumbing, extracting 6-8 million tons in four hundred years. Today, over half the lead produced is used in batteries. The remaining amount is used in cable sheathing, sheet, pipe, foil, tubes, $\text{Pb}(\text{CH}_2\text{CH}_2)_4$, solders, pigments, and chemicals. $\text{Pb}(\text{CH}_2\text{CH}_2)_4$ is used as an antiknock additive in gasoline, but is being phased out by the Environmental Protection Agency.

Most lead is obtained from PbS ore. This is concentrated from low-grade ores by froth flotation, then roasting in air to produce PbO . The PbO is then mixed with coke and limestone, and the mixture is reduced in a blast furnace. The following equations illustrate the process:



Another possible reduction method is to replace the reduction of the roasted ore with fresh ore (PbS):



The "Green Ore" used at the ASARCO lead refinery in East Helena has the following composition:

Table 2. Composition of Lead Green Ore [11]

| Element | Wt. % |
|--|-----------|
| Lead (PbS) | 34-36 |
| Copper (Cu ₂ S) | 3.9-4.1 |
| Arsenic (As ₂ S ₂ , As ₂ S ₃) | 0.8-1.0 |
| Antimony (Sb ₂ S ₃) | 1.1-1.3 |
| Sulfur (as the metal sulfides) | 57.6-60.2 |

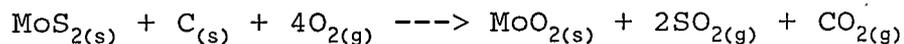
The ASARCO lead refinery in East Helena uses the roasting/blast furnace process. However, they combine the lead ore with regular coke in the initial roasting process to speed up the production of SO₂. The SO₂ is then used to produce sulfuric acid. The purpose of the lead research in this thesis is to determine if petroleum coke could be substituted for regular coke in the initial roasting process.

THEORETICAL ASPECTS

All of the reactions for molybdenum, copper, iron and lead involve rather high temperatures. If petroleum coke is going to be used in the production of the metals in question, it would be useful to know the thermodynamics of the systems. Since the reactions for each experiment are fairly well known, as are the thermodynamic properties for the compounds in question, one can calculate the temperature of neutral equilibrium, the Gibbs standard energy change of reaction, and the heat of reaction. Since the Gibbs standard energy change of reaction must be equal to or less than zero for a feasible reaction, and $\Delta G = 0$ at neutral equilibrium, one can find the feasible temperature range for the reaction (see Thermodynamics of Molybdenum Oxidation). Once a feasible temperature range is known, one can use it to design appropriate experiments and to better evaluate the results of these experiments.

Thermodynamics of Molybdenum Oxidation

Molybdenite is to be converted to molybdenum dioxide by the following reaction:



This reaction is probably not the only reaction taking place when MoS_2 is oxidized to MoO_2 , but it will allow a good estimate of the temperature of neutral equilibrium and the heat of reaction. The following information is available from the Handbook of Chemistry and Physics: [12]

Table 3. Thermodynamic Properties of Some Molybdenum Compounds

| Compound | Standard Entropy cal/deg*mol | Gibbs Standard Energy kcal/mol | Standard Enthalpy kcal/mol |
|----------------|---------------------------------|-----------------------------------|-------------------------------|
| MoS_2 | 14.96 | -54 | -56.2 |
| C | 1.372 | 0 | 0 |
| O_2 | 49.003 | 0 | 0 |
| MoO_2 | 11.06 | -127.40 | -140.76 |
| MoO_3 | 18.58 | -159.66 | -178.08 |
| SO_2 | 59.30 | -71.748 | -70.944 |
| CO_2 | 51.06 | -94.254 | -93.963 |

The heat of reaction is calculated by subtracting the sum of the enthalpies of the reactants from the sum of the enthalpies of the products. A negative quantity indicates an exothermic reaction, a positive quantity means the reaction is endothermic. [13]

$$\text{Heat of Reaction} = \Sigma(\text{Product Enthalpies}) \\ - \Sigma(\text{Reactant Enthalpies})$$

$$\text{Heat of Reaction} = [-140.76 + 2(-70.944) + -93.963] \\ -[-56.2 + 0 + 4(0)]$$

Heat of Reaction = -320.411 kcal/mol

So the reaction is very exothermic.

An approximation of the temperature range at which a reaction is feasible can be determined by calculating the Gibbs standard energy change of reaction and the neutral equilibrium temperature. A proof of this begins with:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \quad (1)$$

The equation for ΔG at one temperature, using ΔH and ΔS at another temperature is:

$$\Delta G_T^\circ = \Delta H_{298}^\circ + \int_{298}^T \Delta C_p^\circ dT - T \left[\Delta S_{298}^\circ + \int_{298}^T \frac{\Delta C_p^\circ}{T} dT \right] \quad (2)$$

Since

$$\Delta C_p^\circ = \sum v_i C_{pi}^\circ \quad (3)$$

If you assume that $C_{p(\text{products})} = C_{p(\text{reactants})}$ then Equation 2 becomes:

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T\Delta S_{298}^\circ \quad (4)$$

It is also know that

$$\Delta G_T^\circ = -RT \ln K \quad (5)$$

If you arbitrarily choose $K = 1$ for a feasible reaction, ($K = 1$ gives about a 50% conversion) then $\ln K = 0$, and Equations 4 and 5 can be combined as:

$$\Delta G_T^\circ \approx \Delta H_{298}^\circ - T \Delta S_{298}^\circ = 0 \quad (6)$$

Equation 6 can be rearranged as:

$$T_{N.E.} = \frac{\Delta H_{298}^\circ}{\Delta S_{298}^\circ} = \frac{H_{\text{prod}, 298}^\circ - H_{\text{react}, 298}^\circ}{S_{\text{prod}, 298}^\circ - S_{\text{react}, 298}^\circ} \quad (7)$$

where $T_{N.E.}$ is the "Temperature of Neutral Equilibrium".

[14]

For the molybdenum reaction, the temperature of neutral equilibrium is:

$$T_{N.E.} = \frac{\frac{1000 \text{ cal}}{\text{kcal}} \left[-140.76 \frac{\text{kcal}}{\text{mol}} + 2(-70.944) \frac{\text{kcal}}{\text{mol}} + -93.963 \frac{\text{kcal}}{\text{mol}} \right] - \frac{1000 \text{ cal}}{\text{kcal}} \left[-56.2 \frac{\text{kcal}}{\text{mol}} + 0 \frac{\text{kcal}}{\text{mol}} + 4(0) \frac{\text{kcal}}{\text{mol}} \right]}{\left[11.06 \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} + 2(59.30) \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} + 51.06 \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} \right] - \left[14.96 \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} + 1.372 \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} + 4(49.003) \frac{\text{cal}}{^{\circ}\text{K}\cdot\text{mol}} \right]}$$

$$T_{N.E.} = 10,131 \text{ } ^{\circ}\text{K}$$

By observation of Equation 5, one can determine that ΔG_r° must be less than or equal to zero for a feasible reaction. The Gibbs standard energy change of reaction is calculated by subtracting the sum of the ΔG_{298}° 's of the reactants from the sum of the ΔG_{298}° 's of the products. [15] A negative quantity indicates a feasible reaction at 298 K, a positive quantity means that the reaction is not feasible.

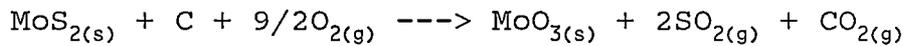
$$\begin{aligned} \text{Gibbs Standard Energy Change of Reaction} &= \Sigma(\Delta G_{298}^{\circ} \text{ Products}) \\ &\quad - \Sigma(\Delta G_{298}^{\circ} \text{ Reactants}) \end{aligned}$$

$$\begin{aligned} \text{Gibbs S.E.C.R} &= [-127.40 + 2(-71.748) + -94.254] \\ &\quad - [-54 + 0 + 4(0)] \end{aligned}$$

$$\text{Gibbs S.E.C.R} = -311.15 \text{ kcal/mol}$$

Since the Gibbs S.E.C.R is negative, the reaction is thermodynamically feasible from 298 K to 10,131 K, the temperature of neutral equilibrium. Note that the compounds in question probably do not exist at 10,131 K, but the thermodynamics state that if they did exist at that temperature, the reaction would be feasible.

In addition, the following thermodynamic properties are calculated for



using the methods outlined above:

Heat of Reaction (ΔH_{298}^f).....-357.64 kcal/mol

Gibbs Energy of Reaction (ΔG_{298}^f).....-343.41 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...7.36 K

Figure 2, Delta G vise Temperature for Oxidation of MoS_2 to MoO_2 , and Figure 3, Delta G vise Temperature for Oxidation of MoS_2 to MoO_3 provide a comparison of the thermodynamic feasibility for the reactions in question.

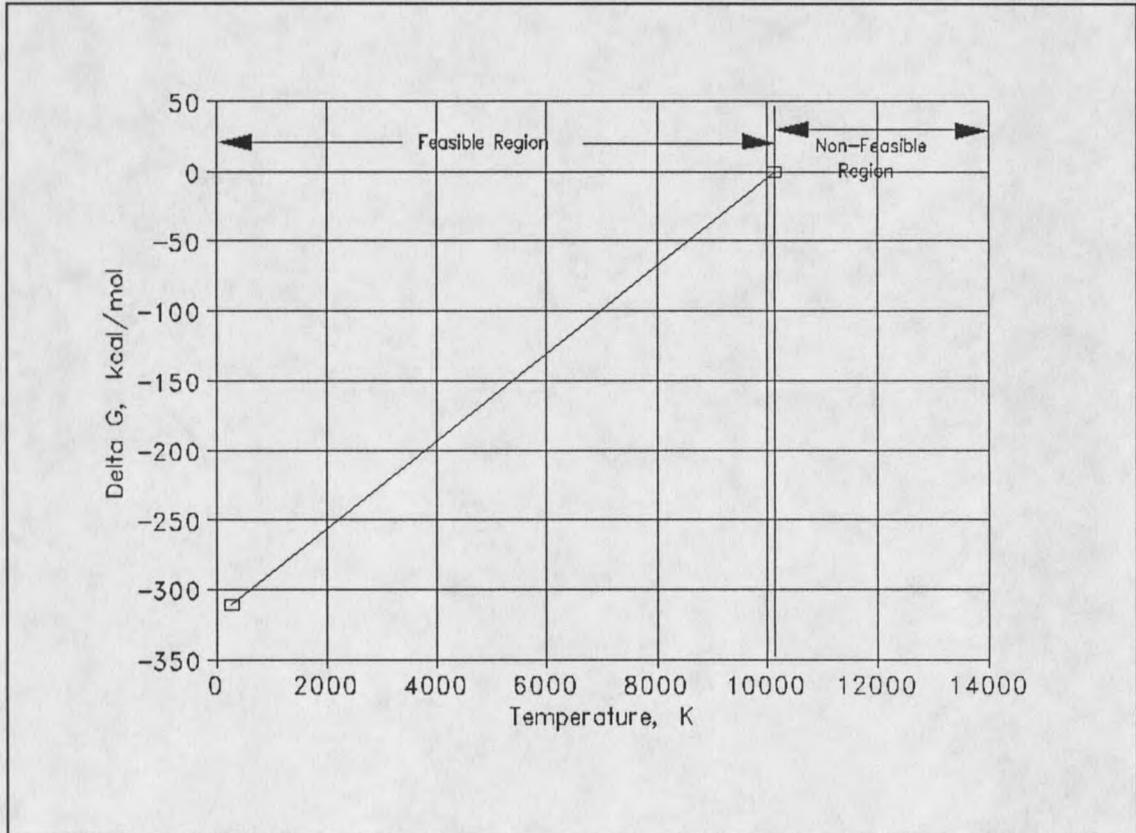


Figure 2, Delta G vs Temperature for Molybdenum Oxidation

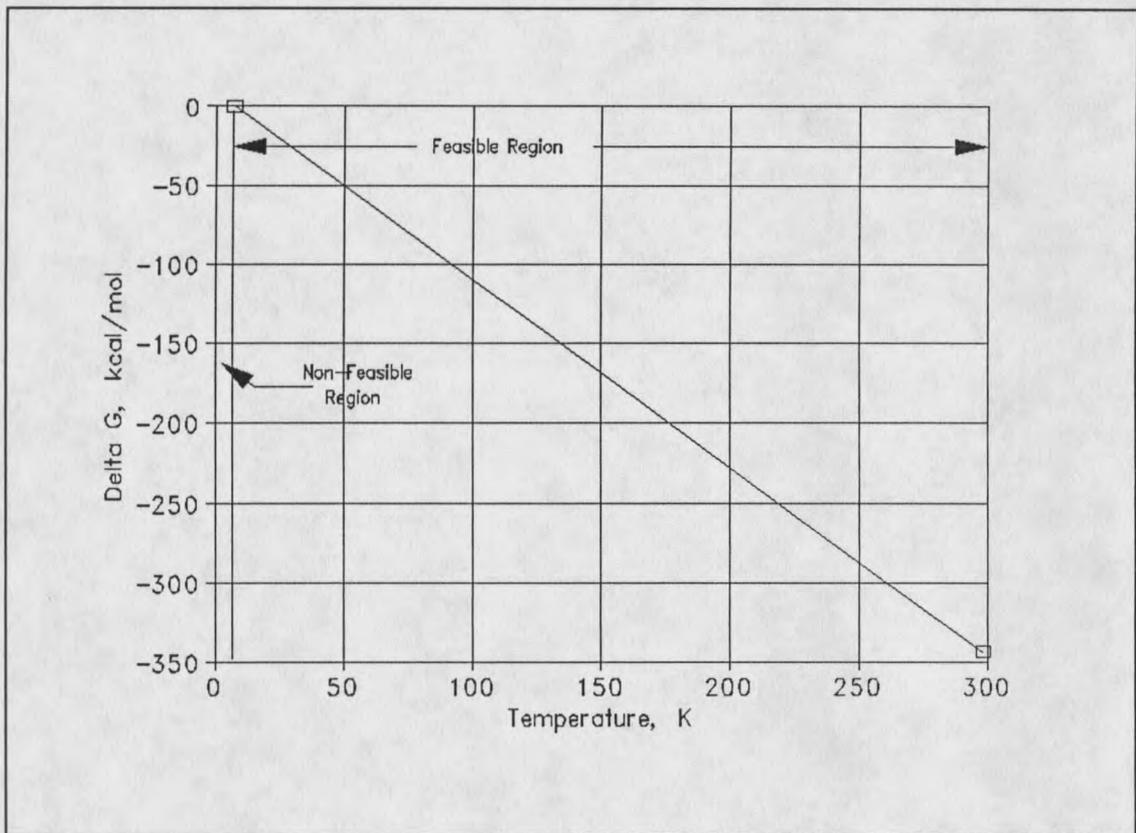
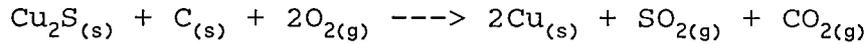


Figure 3, Delta G vs Temperature for Oxidation of MoS_2 to MoO_3

Note that ΔG is more negative at lower temperatures in the $\text{MoS}_2 \rightarrow \text{MoO}_3$ case than in the $\text{MoS}_2 \rightarrow \text{MoO}_2$ case. This shows that it is more thermodynamically feasible for molybdenum ore to oxidize to MoO_3 than to MoO_2 . However, limiting the amount of oxygen would modify reaction conditions to favor oxidizing the ore to MoO_2 , and make $\text{MoS}_2 \rightarrow \text{MoO}_2$ possible.

Thermodynamics of Copper Reduction

Copper ore is converted to blister copper by the following reaction:

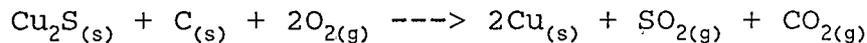


The thermodynamic properties of copper are listed in the Handbook of Chemistry and Physics: [16]

Table 4. Thermodynamic Properties of Some Copper Compounds

| Compound | Entropy cal/deg*mol | Gibbs Standard Energy kcal/mol | Standard Enthalpy kcal/mol |
|-------------------|------------------------|--------------------------------------|----------------------------------|
| Cu ₂ S | 28.9 | -20.6 | -19.0 |
| C | 1.372 | 0 | 0 |
| O ₂ | 49.003 | 0 | 0 |
| Cu | 7.923 | 0 | 0 |
| SO ₂ | 59.30 | -71.748 | -70.944 |
| CO ₂ | 51.06 | -94.254 | -93.963 |
| Cu ₂ O | 22.26 | -34.9 | -40.3 |

The following thermodynamic properties are calculated for



using the methods outlined above:

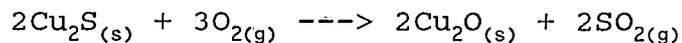
Heat of Reaction (ΔH_{298}^f).....-145.907 kcal/mol

Gibbs Energy of Reaction (ΔG_{298}^f).....-145.402 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...70,418 K

In addition, the following thermodynamic properties are

calculated for



using the methods outlined above:

Heat of Reaction (ΔH_{298}^f).....-184.48 kcal/mol

Gibbs Energy of Reaction (ΔG_{298}^f).....-172.096 kcal/mol

Temp. of Neutral Equilibrium ($T_{N.E.}$)...4.12 K

Both of these reactions are very exothermic. In addition, the Gibbs energy of reaction is negative for both reactions. This means that the reaction $\text{Cu}_2\text{S} \text{ ---> } \text{Cu}$ is feasible for all real temperatures and the reaction $\text{Cu}_2\text{S} \text{ ---> } \text{Cu}_2\text{O}$ is feasible from 4.12 K on up.

The feasibility of making Cu is shown in Figure 4, Delta G vs Temperature for Reducing Cu_2S to Cu:

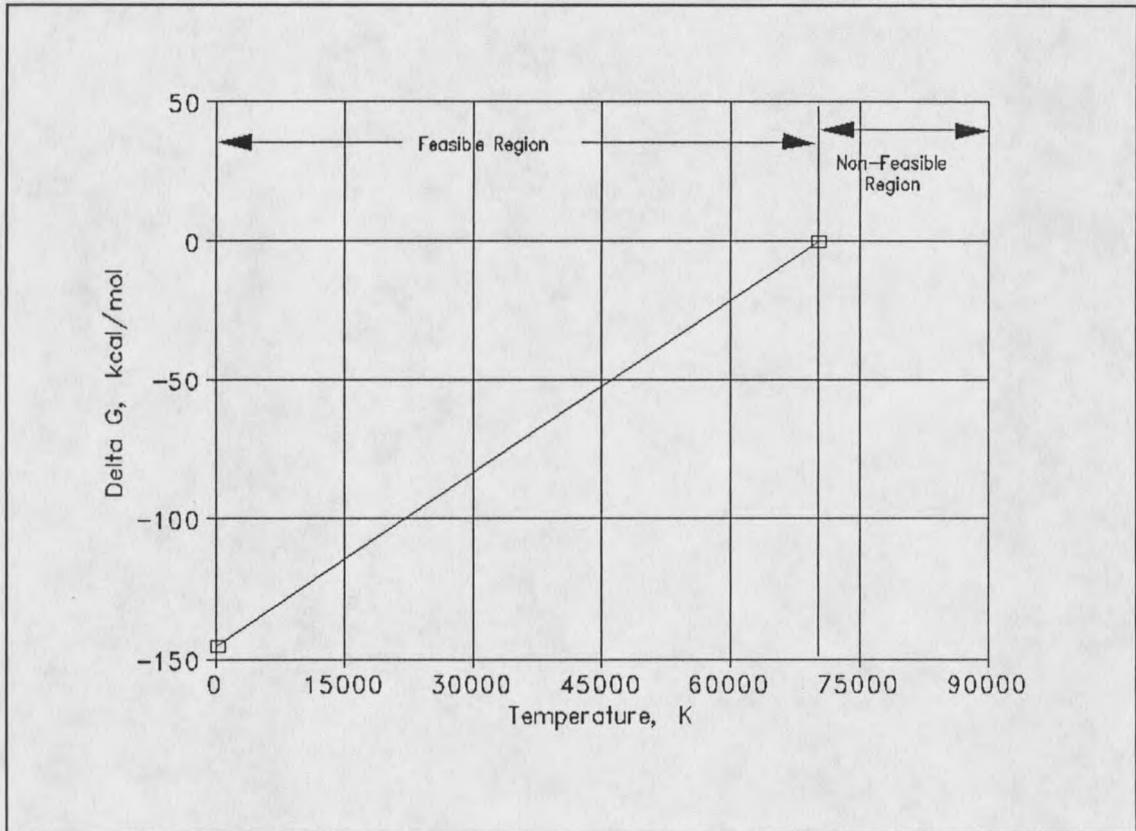


Figure 4, Delta G vs Temperature for Reducing Cu_2S to Cu

