Self Heating of Sulphides: A Thermodynamic Approach

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Self Heating - Introduction

- Sulphide minerals (pyrrhotite, pentlandite, etc.) can spontaneously heat under the right conditions:
  - Presence of moisture
  - Presence of oxygen gas
- This can be hazardous for mining, storage or transportation
  - Given enough heat, the temperature can rise to the point of ignition
- Significant amount of research being done at McGill investigating causes and mitigation methods
- Research and literature suggest two potential causes;
  - Oxidation of the sulphide mineral:
    $FeS_{(s)} + O_{2(g)} \rightarrow (FeO, Fe_2O_3\ Fe_3O_4) + HEAT$
  - Oxidation of H_2S gas:
    $FeS_{(s)} + H^+_{(aq)} \rightarrow H_2S_{(g)}$ + Metal Ions
    $H_2S_{(g)} + O_{2(g)} \rightarrow (S^o, SO, SO_2, H_2SO_4) +$ HEAT

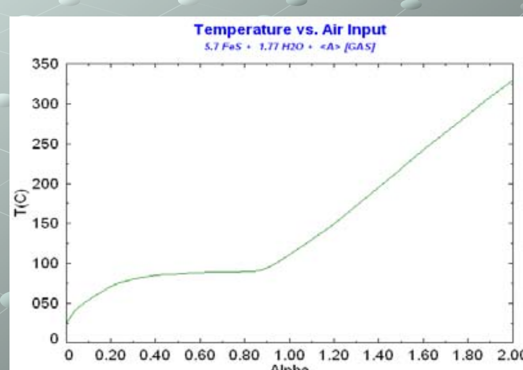
Outline - Scope

- Introduction to self heating and research
- System 1: 'Base' system involving FeS, H_2O and O_2;
  - Investigate temperature variation, solid, liquid and gas phases present
  - Determine reactions occurring
- System 2: Investigate system without moisture; thus without hydrogen
- System 3: Investigate effects of gas stream and $H_2S_{(g)}$ specifically
- System 4: Set up an acidic stream
- System 5: Investigate the effects of acidity and pH control
- System 6: Investigate the effects of shifting moisture content
- Conclusions

System 1: FeS + H_2O + Air(N_2/O_2) Study: Temperature vs. air variation

- System is based on McGill's standard self heating set up; however T_i = 25°C
- 500g of Sulphide → 5.7 mol FeS
- 6% Moisture → 31.9g = 1.77 mol $H_2O_{(l)}$
- Air input is varied in the form of a stream → (A) = 0.79 N_2 + 0.21 O_2
- Delta H held at 0; temperature increase observed

- What are the primary causes of the increase in heat?
- What species are reacting?
- Why is there a 'hold' at about A=0.3-0.9, T=90°C?
- Note: This will be referred to as the 'base' system



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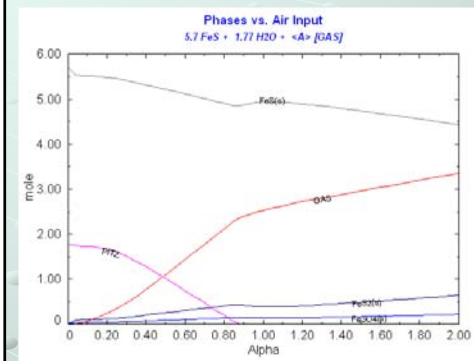
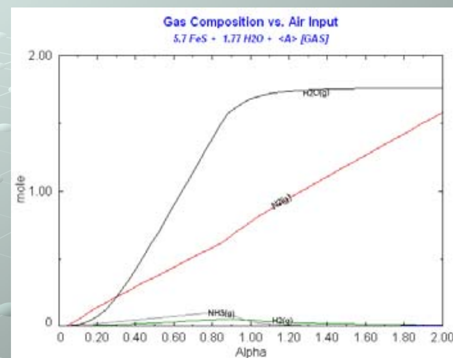
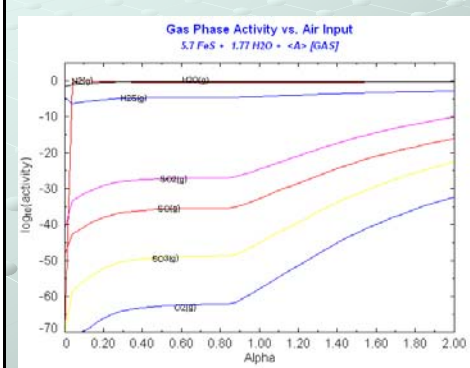


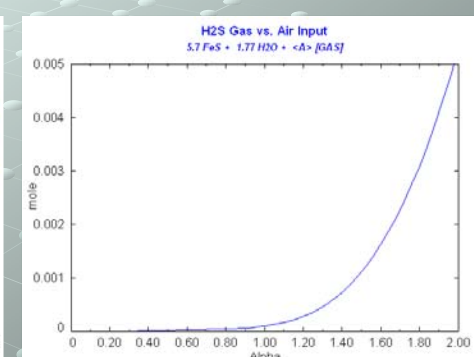


- FeS reactions: Fe → Fe_3O_4; S → FeS_2;
- Oxidation reaction is exothermic and gives off heat → increase in temp
- H_2O is input as liquid (PITZ) → at 90°C heat of oxidation reaction goes to evaporation until the liquid is gone; hence the ‘hold’ until A=0.9
- Once liquid is entirely evaporated, heat continues to increase temp

System 1: FeS + H_2O + Air(N_2/O_2) Study: Temperature vs. air variation

- Extremely low oxygen activity → almost all oxygen forms Fe_3O_4





- Production of $H_2S_{(g)}$ matches increase in temperature; cause or effect?

System 2: FeS + Air(N_2/O_2)
Study: Air variation, no moisture

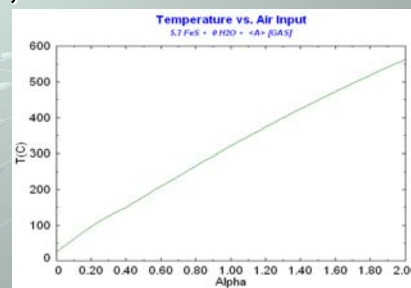
- Temperature increases linearly with air input
- Clearly caused by the oxidation reaction; no interference
- There was no presence of H_2S gas at any point

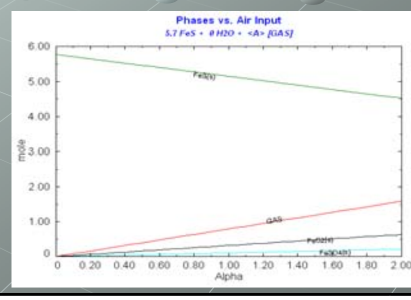
- Slope of T vs. A:

  562–25 / 2-0 = 268°C/mol_{Air}

- Slope of base system after A=0.9:

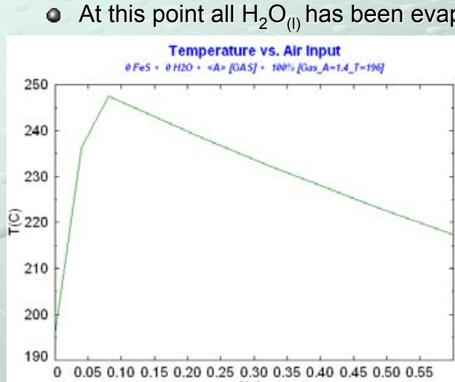
  330–91 / 2–0.9 = 213.4°C/mol_{Air}

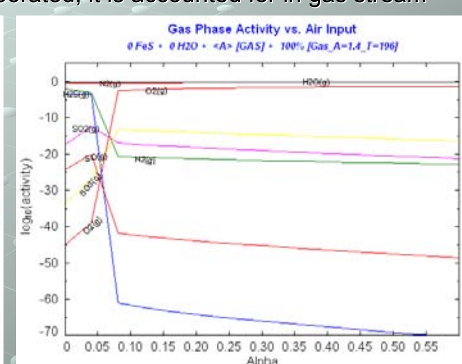




System 3: Gas(H_2S) + Air(N_2/O_2)
Study: Interaction of gas phases

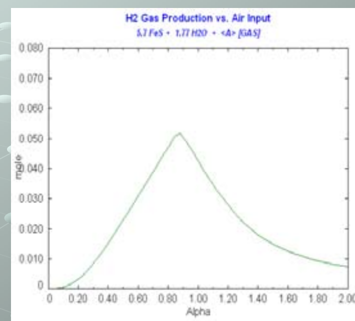
- From base system; take gas stream at A = 1.4, T = 195.89°C
- At this point all $H_2O_{(l)}$ has been evaporated; it is accounted for in gas stream





- Temperature continues to rise with presence of $H_2S_{(g)}$ and $H_{2(g)}$
- Products are a range of SO, SO_2, SO_3; as well as $H_2O_{(g)}$
- Keep in mind that in base system, $H_2S_{(g)}$ and $H_{2(g)}$ would not be depleted

System 3: Gas(H_2S) + Air(N_2/O_2)
Study: Interaction of gas phases



From base system: FeS + H_2O + Air (N_2/O_2)

- Various systems were isolated to attempt to determine their effects;
  - All systems were studied from A=1.4 and T=195.89°C
  - An additional 0.04 mol air was added
  - Temperature was held constant while ΔH was determined for the reaction
- FeS reacting with air: $\Delta H = -4.16*10^3$ J
- Gas phase reacting with air: $\Delta H = -3.86*10^3$ J
- Gas without H_2 reacting with air: $\Delta H = -8.32*10^2$J
- Gas without H_2S reacting with air: : $\Delta H = -3.86*10^3$J

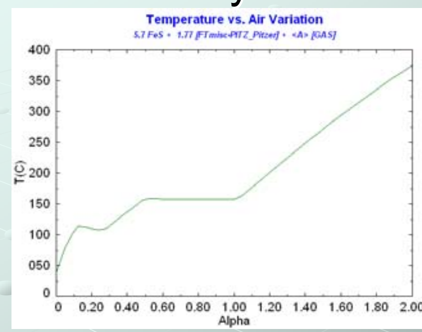
System 4: HCl + H_2O
Study: Heating effect of H^+

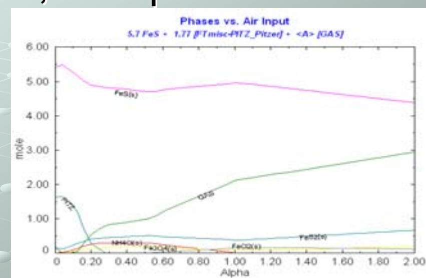
- Proportion of HCl:H_2O varied; reaction temperature and pH determined

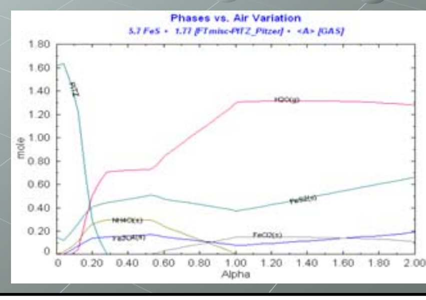
Mol Ratio HCl:H_2O	Reaction Temperature (°C)	Reaction pH
0.000001	25.00	5.643
0.00001	25.00	5.156
0.0001	25.02	4.708
0.001	25.23	4.334
0.01	27.22	4.000
0.03	31.46	3.752
0.06	37.42	3.469
0.1	44.45	3.149
0.2	55.99	2.574
0.225	57.35	2.475
0.25	**58.02**	**2.392**
0.275	57.94	2.325
0.3	57.04	2.275
0.35	48.44	2.303
0.4	36.23	2.356

- Stream with mol ratio of 0.25 was selected, associated pH of about 2.4
- Approximately 23°C of heating can be associated to acid/water reactions

System 5: $FeS + H_2O_{(acid)} + Air(N_2/O_2)$
Study: Air variation, with pH control



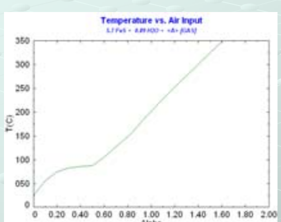


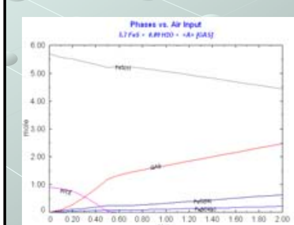


- H^+ and Cl^- interfere with other reactions occurring;
  - NH_4Cl causes decrease in temp
  - Production of $FeCl_2$ and $H_2O_{(g)}$ cause 'hold' at 158°C
- Slope after A=1; 218°C/mol_{Air}

System 6: $FeS + H_2O + Air(N_2/O_2)$
Study: Moisture variation with air variation

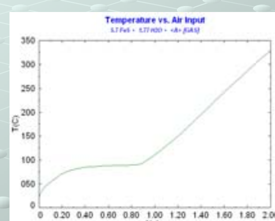
3% Moisture

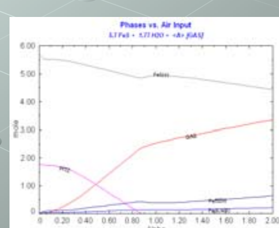




Slope = 233°C/mol_{Air}

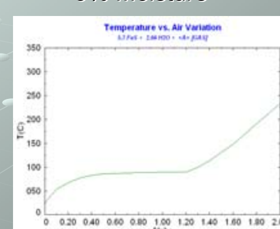
6% Moisture

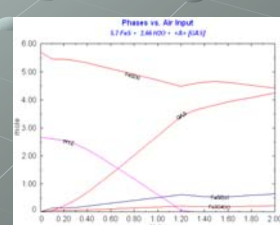




Slope = 213°C/mol_{Air}

9% Moisture





Slope = 179°C/mol_{Air}

Conclusions

- Self-heating of sulphides can be caused by both oxidation of the sulphide and gaseous reactions involving $H_{2(g)}$ and $H_2S_{(g)}$.
- Controlling pH via the addition of HCl results in reactions that may temporarily interfere with the self-heating action; however given sufficient air the temperature will still rise dramatically.
- An increase in moisture content yields a more gradual onset of self heating and ultimately causes less self-heating for a given amount of air.
- Results are based on a thermodynamic approach which has limitations compared to experimental methods.