

Appendix N

The s.p.d.f. Chemical Associates Ltd.

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1.

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TELEPHONE (204) 489-6766

Aug. 16, 2000.

Manitoba Dept. of Labour
200-401 York Ave.
Winnipeg, MB
R3C 0P8

ATTENTION: Mr. Peter Griffin.

Dear Mr. Griffin:

I enclose my report on the HBMS explosion in FlinFlon. This is based solely on the information you provided me and thermodynamic calculations. The invoice is attached. Please let me know if you require any additional information or clarification.

Yours sincerely

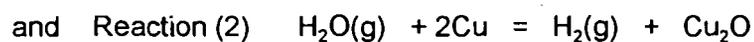
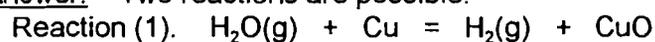


Hyman D. Gesser Ph.D.
Chemist

REPORT ON THE HBMS EXPLOSION IN FLIN FLON MANITOBA.

The Question: Can hydrogen be produced (and cause an explosion) when water is contacted with molten copper at elevated temperatures

The Answer: Two reactions are possible:



Some relevant thermodynamic data are given in Table 1.

TABLE 1. Some Thermodynamic Values for the Reaction of Water with Copper.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K,mol)
H ₂ O (g)	- 241.8	- 228.6	188.7
Cu	0	0	33.1
H ₂	0	0	130.5
CuO	- 157.3	- 129.7	42.6
Cu ₂ O	- 168.6	- 146.0	93.1

Some relevant thermodynamic equations are:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (\text{A})$$

$$\ln K_p = - \Delta G^\circ / RT = \Delta S^\circ / R - \Delta H^\circ / RT \quad (\text{B})$$

$$K_p = P(\text{H}_2) / P(\text{H}_2\text{O})_g \quad (\text{C})$$

I have made the following simplifying assumptions:

- 1) The effects of heat capacity differences between products and reactants is small;
- 2) The pressure of (H₂O)_g i.e., steam, is equal to 1 atm.

Consider Reaction (1)

2

$$\begin{aligned}\Delta S^\circ &= S^\circ(\text{CuO}) + S^\circ(\text{H}_2) - S^\circ(\text{Cu}) - S^\circ(\text{H}_2\text{O})_g \\ &= 42.6 + 130.5 - 33.2 - 188.7 \\ &= 173.1 - 221.9 = -48.8 \text{ J/K, mol}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= \Delta H^\circ(\text{CuO}) - \Delta H^\circ(\text{H}_2\text{O})_g \\ &= -157.3 - (-241.8) = 84.5 \text{ kJ/mol}\end{aligned}$$

From Equation (B):

$$\ln K_p = -48.8/8.31 - 84.5 \times 10^3 / 8.31 T = -5.87 - 10.2 \times 10^3 / T$$

Table 2 presents the calculations for K_p for various values of T

TABLE 2. Values of K_p at Different Temperatures for Reaction (1)

Temp. (°C)	1000	1100	1200	1300	1400
(K)	1273	1373	1473	1573	1673
10200/T	7.99	7.43	6.92	6.48	6.10
ln K_p	-13.86	-13.29	-12.79	-12.35	-11.97
K_p	9.5×10^{-7}	1.6×10^{-6}	2.7×10^{-6}	4.3×10^{-6}	6.3×10^{-6}
P(H ₂) (atm)	9.5×10^{-7}	1.6×10^{-6}	2.7×10^{-6}	4.3×10^{-6}	6.3×10^{-6}

These results show that the equilibrium pressure of H₂ is of the order of a millionth of an atmosphere. Even at a steam pressure of 10 atm, the equilibrium value of the H₂ pressure would be of the order of 10⁻⁵ atm. Hence it is highly unlikely that Rx (1) occurs to the extent of releasing enough hydrogen to cause any damage.

Consider Reaction (2):

$$\begin{aligned}\Delta S^\circ &= S^\circ(\text{H}_2) + S^\circ(\text{Cu}_2\text{O}) - S^\circ(\text{H}_2\text{O})_g - S^\circ(\text{Cu}) \\ &= 130.5 + 93.1 - 188.7 - 33.2 \\ &= 223.6 - 221.9 = 1.7 \text{ J/K, mol}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{Cu}_2\text{O}) - \Delta H_f^\circ(\text{H}_2\text{O})_g \\ &= -168.6 - (-241.8) = 73.2 \text{ kJ/mol}\end{aligned}$$

Using Equation (B):

3

$$\ln K_p = 1.7/8.31 - 73.2 \times 10^3/8.31 T = 0.205 - 8808/T$$

The values used to calculate $P(H_2)$ are listed in Table 3.

TABLE 3. VALUES FOR HYDROGEN FORMED BY REACTION (2)

Temp. °C	1100	1200	1300	1400
K	1373	1473	1573	1673
8808/T	6.42	5.98	5.60	5.26
$\ln K_p$	-6.21	-5.77	-5.39	-5.06
K_p	2×10^{-3}	3.0×10^{-3}	4.5×10^{-3}	6.34×10^{-3}
$P(H_2)$				
$P(H_2O) = 1 \text{ atm.}$	2×10^{-3}	3.0×10^{-3}	4.5×10^{-3}	6.34×10^{-3}
$P(H_2O) = 10 \text{ atm.}$	0.02	0.03	0.045	0.063

NOTE: The percentage of H_2 in the steam is independent of the pressure. The lower explosion limit of H_2 in air is 4% at 1 atm. pressure.

The pressure of hydrogen that can form by reaction (2) when water is contacted with molten copper is significant but less than 1% when the steam pressure is one atm. When the steam pressure is raised to 10 atm the partial pressure of H_2 can be greater but so is the steam. Hence though the Reaction (2) can lead to H_2 , the absence of oxygen in the vicinity of the contact point between the water and copper implies that it is highly unlikely than any hydrogen that could be formed would ignite and cause an explosion.

Based on the above calculations it is my opinion that the explosion was of the BLEVE (Boiling Liquid Expanding Vapour Explosion) or Physical Vapour Explosion type which occurred when the water penetrated the surface slag/flux and on contact with the hot copper was rapidly vaporized causing the explosion.



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Aug. 16, 2000.



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RESEARCH INTERESTS

Physical Chemistry

Gas chromatography; low temperature, atomic and photochemical reactions in the gas phase and on surfaces; electron spin resonance investigation of surface stabilized free radicals; partial oxidation of CH_4 to CH_3OH .

The reactions of free radicals on oxide and semiconductor surfaces and by encapsulation of zeolites. The high pressure catalytic conversion of natural gas to liquid fuels. Passive monitor development for organic pollutants and trace metals in water. Equipment available includes high pressure reactors and an E.S.R. spectrometer.

RECENT PUBLICATIONS

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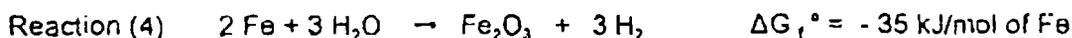
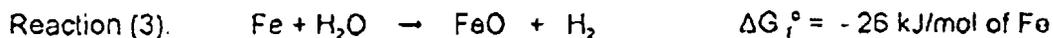
Last updated March 1999 by P. Hultin

2nd REPORT ON THE HBMS EXPLOSION IN FLINFLON MANITOBA.

The iron content of the matte and slag is too high to be all associated with the SiO₂ as Fe₂SiO₄ or other silicates. Hence it is probably also present as FeO, Fe₂O₃ or Fe₃O₄ but is any present Fe. The presence of a magnetic component (magnetite) could be iron (elemental) and not the Fe₃O₄ as implied.

Thus based on the chemical analysis it would appear that there may be elemental iron (perhaps partially dissolved in the molten copper).

Any elemental iron can react with water as follows:



Both reactions can occur at 25°C but because of the negative entropy of each reaction the tendency to react is reduced at elevated temperatures. Thermodynamics can show if enough hydrogen can be produced at the high temperatures.

Table 2. Some Thermodynamic Values for the Reaction of Water with Iron.

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K.mol)
H ₂ O (g)	-241.8	-228.6	188.7
H ₂	0	0	130.5
Fe	0	0	27.3
FeO	-272	-251	60
Fe ₂ O ₃	-824	-742	87.4

Using equations (A), (B), and (C) from report # 1, and
 for Reaction (4) $K_p = \frac{P(H_2)^3}{P(H_2O)^3}$ (D)
 and $P(H_2) = K_p^{1/3} \cdot P(H_2O)$ (E)

For Reaction (3) $\Delta S^\circ = S^\circ(H_2) + S^\circ(FeO) - S^\circ(H_2O) - S^\circ(Fe)$
 $= 130.5 + 60 - 188.7 - 27.3$
 $= -26 \text{ J/K.mol of Fe}$
 $\Delta H^\circ = \Delta H_f^\circ(FeO) - \Delta H_f^\circ(H_2O)$
 $= -272 - (-241.8)$
 $= -30.2 \text{ kJ/mol of Fe}$

From Equation (B), $\ln K_p = -26/8.314 - (-30,200/8.314 T) = -3.13 + 3632/T$

Temp	$\ln K_p$	K_p	$P(H_2)$ (For $P(H_2O) = 1$ atm)
737 °C, 1000K	0.502	1.65	1.65 atm
1037 1300K	-0.333	0.716	0.716 atm
1237 1500K	-0.706	0.50	0.50 atm

The formation of hydrogen under these conditions is highly probable.

For Reaction (4):

$$\begin{aligned} \Delta S^\circ &= 3 S^\circ(H_2) + S^\circ(Fe_2O_3) - 2 S^\circ(Fe) - 3 S^\circ(H_2O) \\ &= 391.5 + 87.4 - 54.6 - 566.1 \\ &= -141.8 \text{ J/K.mol} \\ \Delta H^\circ &= \Delta H_f^\circ(Fe_2O_3) - 3 \Delta H_f^\circ(H_2O) \\ &= -82.4 - 3(-241.8) = -98.6 \text{ kJ/mol} \end{aligned}$$

$$\ln K_p = 141.8/8.314 + 98,600/8.314T = -17.06 + 11859/T$$

Temp	$\ln K_p$	K_p	$P(H_2)$ (for $P(H_2O) = 1$ atm)
737°C 1000 K	-5.2	5.5×10^{-3}	0.18 atm
1037 °C 1300 K	-7.9	3.6×10^{-4}	0.07 atm
1237°C 1500 K	-9.15	1.1×10^{-4}	0.047 atm

This reaction (4) does not produce enough hydrogen at the higher temperatures to be a significant hazard.

I must check the library again for more information on the copper/iron system.


H.D. Gesser
Sept. 21, 2000

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REPORT #3 ON THE HBMS EXPLOSION IN FLINFLON MANITOBA

On Monday evening, Sept. 25, 2000, I spoke to Skip Hills from HBMS. Based on the discussion we had it would seem that iron is added as cast iron at the bottom of the crucible when it is first loaded with ore. Hence it is unlikely that free iron is present in the slag or matte on the top of the melted copper. Thus the direct reaction of elemental iron with water or steam to produce hydrogen is highly improbable. There is no other component in the system that can produce hydrogen directly from water or steam under the conditions that prevailed.

However, the phase diagram of the copper/iron system attached shows that some iron is soluble in the molten copper and therefore is a potential source for the reduction of steam to hydrogen. This would involve a gas (H_2O_g) reacting with the surface of the liquid metallic solution (Cu/Fe), which at temperatures greater than $1100^\circ C$ would be slow and I do not believe that this reaction could proceed at any significant extent because any iron oxide formed would prevent further reaction of the steam with dissolved iron. I also believe that any hydrogen that could form would not have any oxygen with which to react explosively because the steam would have displaced the oxygen leaving any hydrogen to diffuse away rapidly without reacting.

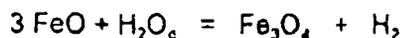
I conclude, as in my first report, that the explosion was caused by rapid evaporation of water used to cool the melt.

H. D. Gesser
Chemist
Sept. 26, 2000

SUPPLEMENT:

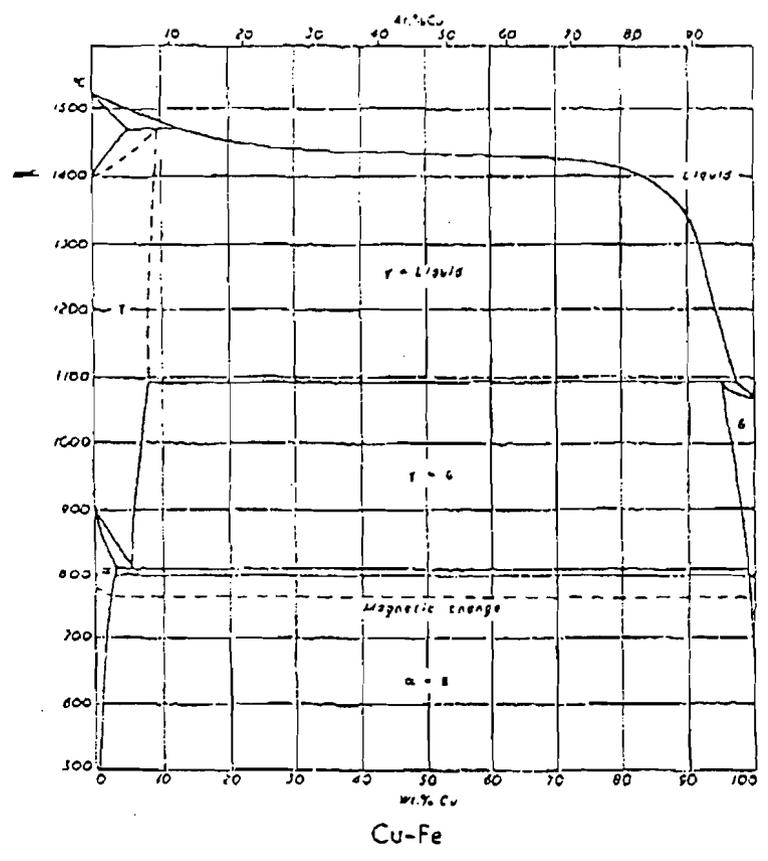
The presence of magnetite, Fe_3O_4 or $FeO \cdot Fe_2O_3$ implies that some FeO is formed or present in the system.

The reaction:



can occur. The reaction has been postulated to occur in the blast furnace and preliminary calculation indicate that at $1100^\circ C$ it is possible to obtain 5% H_2 and at $1200^\circ C$ the H_2 is 3%. This should be verified by a further literature search.

H.D. Gesser



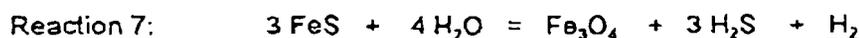
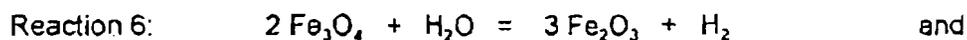
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REPORT # 4 ON THE HBMS EXPLOSION IN FLINFLON MANITOBA

A search of the literature on equilibrium reactions which occur in blast furnaces for iron production has revealed two other potential reaction which can produce hydrogen (besides reaction # 5 given in Report # 3—Supplement) by the reaction with steam. These are:



Using the thermodynamic data from Tables 2 and 3 it was possible to calculate the amount of hydrogen which can be produced.

Table 3. Some selected thermodynamic values;

Substance	ΔH_f (kJ/mol)	ΔG_f (kJ/mol)	S° (J/K.mol)
Fe_3O_4	-1118.4	-1015.4	146
FeS	-100.0	-100.4	60.3
H_2S	-20.6	-33.6	205.7

Using equations A, B, and C from Report # 1 the calculated values of K_p are given in Table 4.

Table 4. Some values of K_p for equations 6 and 7.

Equation	1000°K	1100°K	1200°K	1300K	1400K
#6	1.07×10^{-5}	1.15×10^{-5}	1.2×10^{-5}	1.3×10^{-5}	1.37×10^{-5}
#7	1.84×10^{-7}	4.8×10^{-7}	1.04×10^{-6}	2.06×10^{-6}	3.66×10^{-6}

These equilibrium constants are too low to produce any significant amount of hydrogen when the partial pressure of steam is not greater than 1 atm. Only reaction 5 (Report #3) is capable to producing hydrogen in the range of the explosion limits in air, viz. 4% to 75% in air.

It has to be realized that the thermodynamic calculations are for equilibrium conditions and do not give any information as to the rate at which the equilibrium values can be achieved, if ever. Thus even if thermodynamics predicts that the concentration of hydrogen can reach 5% (i.e., above the lower explosion limit in air) it does not necessarily ever achieve this value and it must be further taken into consideration that the displacement of air by steam will reduce the probability of a hydrogen-air explosion.

I therefore believe that hydrogen was not involved in the HBMS explosion for the several reasons given above and are summarized below:

1. Of the reactions which could occur in the system only one (reaction # 5) can produce hydrogen in amounts which are capable of causing an explosion in air at one atmosphere. However since the steam would have displaced the air the chance of a hydrogen explosion is most unlikely.
2. Thermodynamics can only predict the maximum yields of a product under equilibrium conditions (in a closed system) but gives no kinetic rate at which the equilibrium can be achieved.
3. Hydrogen is the lightest gas known and the molecules move with the highest speed. It therefore diffuses very rapidly and seldom causes an explosion in an open environment.
4. In each of the seven reactions considered in these 4 reports, the reactions are of the type: $(\text{Solid})_1 + \text{H}_2\text{O} = (\text{Solid})_2 + \text{H}_2$ except for reaction # 7 where an additional gas, H_2S , is produced. This type of reaction seldom goes to completion because the product solid is formed on top of the reactant solid and shields further reaction of the gas with the reactant. This type of interference is also known to occur when a solid reacts with a liquid to form another solid product and another liquid, e.g., batteries of the Ni/Cad type and is known as a memory effect.

CONCLUSION

My conclusion is identical to that reached at the end of Report # 1. The explosion was of the BLEVE (Boiling Liquid Expanding Vapour Explosion) or the Physical Vapour Explosion.



H. D. Gesser
Chemist
Sept. 29, 2000