Lecture 8: Thermo chemistry applications in metal extraction

Contents

Problem 1 : Carbothermic reduction

Carbothermic reduction is commonly used to produce metals from oxides. Calculate the heat required (in Kcal/Kg of Zinc) to produce Zinc from reduction of ZnO with carbon.The reactants, ZnO and C, enter at 250°C , whereas Zinc vapor and CO gas leave at 1027°C .use the following data:

$$\mathrm{Zn\ (S)\ =\ Zn\ (1);\ Tm\ = 692.5K;}\ \Delta H_{fusion} = 1740\ \mathrm{cal\ /g.mole}$$

$$\mathrm{Zn\ (1)\ =\ Zn\ (g);\ Tm\ = 1180K;}\ \Delta H_{Vap} = 27565\ \mathrm{cal\ /g.mole}$$

Components	ΔH° (Cal/g.mol)	Cp (Cal/g.mol. K)
ZnO(S)	-83800	$11.71+(1.22 \times 10^{-3}\ T) -(2.18 \times 10^{5}\ T^{-2})$
C(S)	0	$0.026+(9.307\times10^{-3}\ T)- (0.354\times10^{5}\ T^{-2})$
Zn(S)	0	$5.35+(2.40\times10^{-3}T)$
CO(g)	-26420	$6.79+(0.98\times10^{-3}T)-(0.11\times10^{5}\ T^{-2})$
Zn(1)	----	7.50
Zn(g)	--------	5.00

Solution:

$$\mathrm{ZnO(S)\ +\ C\ (s)\ =\ Zn\ (g)\ +\ CO\ (g)}$$

Reactants are at 298 K and products at 1300 K

$$(\Delta H_R)_{1300K} = \Delta H°_{298} + \sum(H_{1300} - H_{298})p - \sum(H_{1300} - H_{298})R \qquad 1$$

Reactants are at 298K; hence sensible heat in reactants is zero

To calculate heat content in products, following scheme may be adopted

$\text{Zn}\ (298)\ =\ \ \text{Zn}\ (692.5);\ \text{sensible heat}$

$\text{Zn}\ (692.5\text{K}) =\ \ \text{Zn}\ (692.5\ \text{K});\ \text{Latent heat of fusion},\ \text{Zn}\ (\text{L}), 692.5\ =\ \text{Zn}\ (\text{l}).1180\ \text{K}\ \ \text{sensible heat}$

$\text{Zn}\ (1180)\ \ \ =\ \ \text{Zn}\ (\text{v})\ ;\ \text{latent heat of evaporation}$

$\text{Zn}\ (\text{v})\ 1180\ \text{K} =\ \ \text{Zn}\ (\text{v})\ \ 1300\text{K}\ ;\ \text{Sensible heat.}$

Sensible heat in CO at 1300K = $\int_{298}^{1300} \text{cpdt}$

Heat of reaction at 298 K = $57380 \frac{\text{cal}}{\text{gmol}}$

Performing calculations on sensible heat of products by using C_p value and putting these values in equation 1 $(\Delta H_R)_{1300K}\ = 101081\ \frac{\text{cal}}{\text{gmol}} = 1555.1\ \frac{\text{keal}}{\text{kgZn}}$

Atomic weight of Zinc = 65

Problem 2: **Heat of reaction in extraction of Zn**

Calculate ΔH at 1250 K for the following reaction

$\text{ZnS(s)} +\ \text{CaO(s)} + \text{C(s)}\ \ =\ \text{Zn(g)}\ +\ \text{CaS(s)} + \text{CO(g)}$. Use the data of problem 1 for latent heats

Components	ΔH° (cal/g.mol)	Cp (cal/g.mol K)
CO(g)	-26420	$6.79+(0.98\text{x}10^{-3}\text{T}) - (0.11 \text{ x } 10^{5}\text{T}^{-}2)$
Zn(1)	------	7.50
Zn(g)	------	5.00
ZnS(S)	0	$5.35 + (2.40 \text{ x } 10^{-3}\text{T})$
C(S)	-----	$4.10 + (1.02 \text{ x } 10^{-3}\text{ T}) - (2.10 \text{ x } 10^{5}\text{T}^{-2})$
ZnS(S)	-48200	$12.16+(1.24\text{x}10^{-3}\text{T})-(1.66 \text{ x } 10^{5}\text{ T}^{-2})$
CaO	-151600	$11.86+(1.08 \text{ x } 10^{-3}\text{T})-(1.66 \text{ x } 10^{5}\text{ T}^{-2})$
CaS	-110000	$10.20+(3.8 \text{ x } 10^{-3}\text{ T})$

Solution :

First calculate $\Delta H°_{298} = 63380 \frac{\text{cal}}{\text{g.mol}}$

Now calculate sensible heat in products .The products are raised from a reference temperature 298 k to 1250 K .Use respective Cp values and integrate from 298 K to 1250 K.

$$\Delta H_{\text{products}} = 55559 \frac{\text{cal}}{\text{g.mol}}$$

Similarly $\Delta H_{\text{reactnts}} = 27733 \frac{\text{cal}}{\text{g.mol}}$

$$(\Delta H_R)_{1250} = 91206 \frac{\text{cal}}{\text{g.mol}}$$

Problem 3: Electric melting

An electric melting furnace is used to melt copper scrap .The scrap is initially at 25°C .The overall power consumption is 300 kW -hr /ton of molten copper ,when heated to a temperature of 1523 K. Estimate the thermal efficiency of this furnace . melting point of copper 1356 K, Latent heat of melting =12970 J/g. mole

$$\text{Cp(solid Cu)} = 22.64 + \frac{(6.28 \text{ x } 10 \ -3 \text{ T})}{\text{g}} \frac{\text{J}}{\text{g. mole K}} \quad \text{Cp(liquid Cu)} = 31.38 \frac{\text{J}}{\text{g. mole K}}$$

Solution:

To estimate thermal efficiency,one has to calculate theoretical power consumption in heating scrap from 298 K to 1523 K.

Power required = sensible heat required to raise scrap temperature from 298 K to 1356 K + Latent heat of melting + sensible heat to raise temperature of liquid copper from 1356 to 1523 K.

Power required theoretically = 208.5 kw-hr /ton of copper and thermal efficiency = 69.5%

Problem 4: Heat of formation of compound

Given the following heats formation (in cal /g.mole):

$$(\text{Ca, Si, 2O}) = -25200$$

$$(\text{Ca, Si, 3O}) = -377900$$

$$(\text{Si, 2O}) = -201000$$

Write each of these in the form of a thermo chemical equation .From these equations determine the heat of formation of CaO per kilogram of Ca.

This type of problem is very useful in metal extraction .In cases when heat of formation of a compound is not known, then it can be determined from the heat of formation of different stepwise reactions leading to formation of compound.

In the above problem one has to find heat of formation of CaO

Let us form the Thermo chemical equations:

$$CaO + SiO_2 = CaSiO_3; \quad \Delta H^\circ = -25200 \quad (1)$$

$$Ca + Si + 3O = CaSiO_3; \quad \Delta H^\circ = -377900 \quad (2)$$

$$Si + O_2 = SiO_2; \quad \Delta H^\circ = -201000 \quad (3)$$

Subtraction equation 1 and 3 from equation 2, w.ge 1

$$Ca + O = CaO$$

$$\Delta H_{298^\circ} = -15700 \ \mathrm{cal/g.mol}$$

$$= -3.8 \times 10^3 \ \mathrm{kcal/KgCa}$$

Problem of 5: Heat of formation of compound

Given the following heats of formation

$(Fe, O) = 1151 \mathrm{cal/g\ of\ Fe}.$

$(S, 3O) = 2930 \ \mathrm{cal/g\ of\ S}.$

$(Fe, S, 4O) = 1456 \ \mathrm{cal/g\ of\ FeSO4}.$

Required the molar heat of formation of FeSO4. from FeO and SO_3

Now you can try this problem and get heat of formation of $FeSO_4 = 63.1 \frac{\mathrm{kcal}}{\mathrm{gmol}}$

Problem 6: Production of silicon carbide

Calculate the heat of the reaction for production of silicon carbide:

$$SiO_2 + 3C = SiC + 2CO$$

The reactants and products are at 1973 K.

Components	ΔH° (J/g.mol)	Cp (J/g.mol K)
SiO2	–841386	46.945 + 34.309 x 10^{-3} T –11.297 x 10^{5} T^{-}2)
C	--------	17.154 + 4.268 x10
Sic	–117208	109.266 + 14.67 x 10^{-3}T – 39.468 x $10^{5}$$T^{-}$2)
Co	–112352	28.409+4.1x10^{-}3 T–0.460 x $10^{5}$$T^{-2}$)

Problem of this type are illustrated .Practice it to calculate heat of reaction $= 565.945 \frac{\mathrm{kJ}}{\mathrm{gmol}}$

Problem 7: Electric furnace to produce CaC_2

An electric furnace is used to produce CaC_2 as per the following reaction:

$CaO + 3C = CO + CaC_2$

Power consumption is 4 kilowatt -hour /Kg of CaC_2.The CaC_2 reacts with H_2O according to the reaction

$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$

Given ΔH° (Keal /Kg. mol) $CaC_2 = -14600$, and $CO = -26840$

$CaO = -151600$

Mean heat capacity of cold water =0.53cal/g° C

Required:

1. The minimum Power to produce 1 ton of CaC_2 per hour.
2. The electro – thermal energy efficiency of the furnace operation.
3. If 200 g. of CaC_2 is treated with 20 kg. Of cold H_2O , calculate the rise in temperature?

Calcium carbide is a very important regent and is used to desulphurize pig iron.

You can try; the answers are:

A) 2001.4 kwh/ton CaC_2
B) 50%
C) 4.3°C.

Problem 8 Hall Heroult cell

Calculate the heat of the reaction taking place in the Hall-Heroult cell at a temperature of 1000°C

$Al_2O_3 + 3\ C = 2A\ l + 3CO$

Although this temperature is below the melting point Al_2O_3, the alumina is actually dissolved in molten cryolite .Assume, therefore that heat content of the Al_2O_3 includes its heat of fusion .Heat of fusion of Al_2O_3 and Al is 1046.5 and $1004.6\ J/g.mol$ S respectively .Melting point of Al is $659°C$.

Components	ΔH° (J/g.mol)	Cp (J/g.mol K)
Al_2O_3	-380000	$106.608 + 17.782\ x10^{-3}T-28.535x10^{5}T^{-}2$
C	----------	$17.154+4.268x10^{-3}T-8.786x10^{5}T^{-}2$
Al(s)	---------	$20.669+12.385x10^{-3}T$
Al(1)		31.798
CO	-26840	$28.409 + 4.1\ x10^{-3}T – 0.460\ x\ 10^{5}T^{-}2$

The above problem has a relevance in electrolytic reduction of Al_2O_3 to produce Al. Hall- Heroult cell is widely used to produce aluminum.

Heat of reaction $= 1241.911\ kg/\ mol.$

Problem 9: Heat of Formation

Will heat of formation be different when a compound forms A) From two different compounds and (b) when if forms from pure elements.

<u>**Answer;**</u> Heat of formation will be different .For example Heal of formation of $CaCO_3 = -289500\ kcal$ when formed from elements Ca, C and O

Heat of formation is $+43450$ kcal when $CaCO_3$ forms from CaO and CO_2.