Thermochemistry and its application in Metallurgy.

(* Thermochemistry: The study of heat changes in chemical reactions.

(* exothermic reaction: The heat accompanying ~~this~~ this reaction is large and negative

Ex $2Al + \frac{3}{2}O_2 = Al_2O_3$ $\Delta H = -1674{,}000$ J/mol

(* Endothermic reaction: The heat energy change accompanying of this reaction will be positive

Ex
Carbon is used to reduce zinc oxide in the commercial extraction of zinc and the reaction can be represented as:

$ZnO + C = Zn + CO$ $\Delta H = +349{,}000$ J/mol

ΔH

reactants and products

ΔH

$\Delta H_{298\,K}$ ΔH_{T}

(1) Heat of Reaction: the change in enthalpy when the amount of reactants in moles shown by the balanced equation for a reaction react completely as shown in the equation

An example of the heat of reaction at 727 C

$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$ $\Delta H = -46{,}700$ J/mol

This is the heat evolved at constant pressure when 3 moles of ~~Fe~~ haematite are reduced by 1 mole of carbon monoxide to form 2 moles of magnetite and 1 mole of carbon dioxide

$3Fe_2O_{3(s)} + CO_{(g)} = 2Fe_3O_{4(s)} + CO_{2(g)}$ $\Delta H = -46.7$ KJ/mol

S → solid
L → liquid = water
(G) gases

(1)

② Heat of formation of compound: The change in enthalpy when 1 mole of compound is formed from its constituent element in their stable forms at 25°C and 1 atm pressure. For example, the heat of formation of lead sulphide:

$$Pb_s + \frac{1}{2} S_{2s} = PbS_s \qquad \Delta H_{298} = -94.1 \text{ kJ}$$

the heat content of element in their standard states at equilibrium at 25°C and 1 atm pressure to be zero.

In above example, the heat content of the lead and sulphur is zero and the heat content of the lead sulphide is −94.1 kJ

$$\Delta H^{o}_{298} = \sum H^{o}_{298,P} - \sum H^{o}_{298,R}$$

$$= -94.1 - (0+0) =$$

another example ⇒

$$2PbS + 3O_2 = 2PbO + 2SO_2 \qquad \Delta H_{SO_2} = -297.1$$

$$2(-94.1) \qquad 2X \qquad 2(-297.1)$$

Given $\Delta H_{298} = -845.2$ kJ for reaction; calculate the heat content at 298 K of PbO

$\Delta H_{298} = -94.1$ for PbS

$$\Delta H^{o}_{298} = \sum H^{o}_{298,P} - \sum H^{o}_{298,R}$$

$$-845.2 = 2X + (2 \times -297.1) - (2 \times -94.1 + 0)$$

$$-845.2 = 2X - 594.1 + 188.2$$

$$\therefore X = -219.7 \text{ kJ/mol of PbO}$$

③ Heat of combustion of a substance: The enthalpy change when 1 mole of the substance (an element or compound) is completely burnt in oxygen. For example:

$$Mg + \frac{1}{2} O_2 = MgO \qquad \Delta H_{298} = -602.5 \text{ kJ}$$

$$C + O_2 = CO_2 \qquad \Delta H_{298} = -393.7 \text{ kJ}$$

التحول

(4) Heat of Transformation: The change in enthalpy when 1 mole of a substance undergoes a specific physical change such as (melting, evaporation, allotropic modification), can be given by the symbol L_t.

Latent heat of fusion L_f

Latent heat of evaporation (L_e)

$T_2 > T_t$ [illegible] T_t

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_t} \Delta C_p (T_1 - T_t)\, dt \pm L_t + \int_{T_t}^{T_2} \Delta C_p (T_t - T_2)\, dt$$

(5) Heat of Solution: When one substance dissolves in another there will be a change in enthalpy. This called the heat of solution, and depends on the concentration of the solution which should be stated.

[illegible]

Hess's law of constant heat summation: The overall heat change for a chemical reaction is the same whether it takes place in one or several stages, provided the temperature and either the pressure or the volume remain constant.

(6) In the extraction of Zinc by carbon reduction of Zinc oxide under the basic reaction could be ⇒ $ZnO_s + C_s = Zn_s + CO_g$ at room temperature

but the reaction will not proceed at room temperature and the reduction is carried out at about 1100 °C. Zinc melts at 420 °C (انصهار) and boils at 907 °C (غليان), so assuming that the reaction is carried out at 1 atm pressure, the reaction will be

$$ZnO_s + C_s = Zn_g + CO_g$$

The problem [illegible] the heat of formation of reactants and products at 25 °C, the relationship between their heat capacities and temperature with range 25 - 1100 °C, and the latent heat of fusion and evaporation of Zinc.

Calculate the heat of reaction at 25 °C and at 1100 °C.

Given

Heats of formation at 25 °C

$ZnO_{(s)}$ $\Delta H_{298} = -345{,}100$ J

$C_{(s)}$ $\Delta H_{298} = 0$

$Zn_{(s)}$ $\Delta H_{298} = 0$

$CO_{(g)}$ $\Delta H_{298} = -110{,}500$ J

Heat of Transformation of Zinc

$L_f\ Zn = 7280$ J/mol at 693 K (420 °C)

$L_e\ Zn = 114{,}200$ J/mol at 1180 K (907)

Heat capacities (C_p) in J/mol·K

$ZnO_{(s)} = 48.99 + 5.10 \times 10^{-3}T - 9.12 \times 10^{5} T^{-2}$

$C_{(s)} = 17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^{5} T^{-2}$

$Zn_{(s)} = 22.38 + 10.04 \times 10^{-3} T$

$Zn_{(l)} = 31.38$

$Zn_{(g)} = 20.79$

$CO_{(g)} = 28.41 + 4.10 \times 10^{-3} T - 0.46 \times 10^{5} T^{-2}$

To calculate the heat of reaction at 1100 °C, we use the integrated form of Kirchhoff's equation

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

where ΔC_p = difference in C_p (products (x mole) − Reactants (x mole))

(*) where there is change in state in one of the products or reactants the heat transformation L_t must be subtracted from the total if a reactant transforms, added if a product transforms.

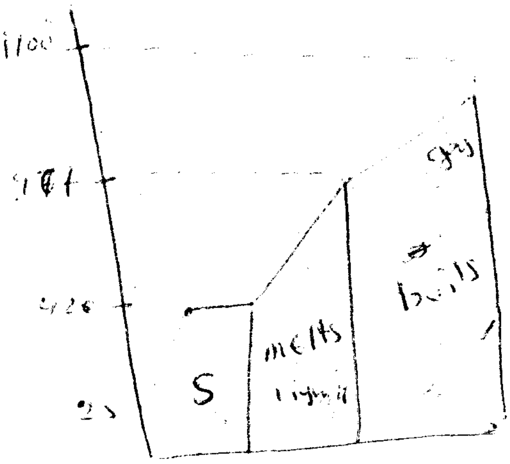
In G.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_t} \Delta C_{p_I} \cdot dT + L_t \int_{T_t}^{T_2} \Delta C_{p_{II}} \cdot dT$$

where T_t is transformation temperature and ΔC_{p_I}, $\Delta C_{p_{II}}$ are the values of ΔC_p below and above the transformation temperature respectively.

$$\Delta H_{1373} - \Delta H_{298} = \int_{298}^{693} \Delta C_{P_I} \cdot dT + L_f Zn + \int_{693}^{1180} \Delta C_{P_{II}} \cdot dT + L_e Zn$$

$$+ \int_{1180}^{1373} \Delta C_{P_{III}} \cdot dT$$



(*) To calculate ΔH_{298}

$$\Delta H_{298} = \sum \Delta H_{product} - \sum \Delta H_{reactants}$$

$$= (\Delta H_{Zn} + \Delta H_{CO}) - (\Delta H_{ZnO} + \Delta H_{C})$$

$$= (0 - 110,500) - (-348,100 + 0)$$

$$= 237,700 \text{ J.}$$

(*) To calculate $\int_{298}^{693} \Delta C_{P_I} \cdot dT$

$$\Delta C_{P_I} = (C_p Zn(s) + C_p(CO)) - (C_p ZnO + C_p C)$$

$$= (22.38 + 10.04 \times 10^{-3} T + 28.41 + 4.10 \times 10^{-3} T - 0.46 \times 10^{5} T^{-2}$$

$$- (48.99 + 5.10 \times 10^{-3} T - 9.12 \times 10^{5} T^{-2} + 17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^{5} T^{-2})$$

$$= -15.36 + 4.77 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}$$

$$\int_{298}^{693} \Delta C_{P_I} \cdot dT = \int_{298}^{693} (-15.36 + 4.77 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}) \, dT$$

$$= \left[-15.36 T + 2.385 \times 10^{-3} T^2 - 17.45 \times 10^{5} T^{-1} \right]_{298}^{693}$$

$$= [-12,000] - [-10,200]$$

$$= -1800 \text{ J}$$

To calculate $\int_{693}^{1180} \Delta C_{P_{II}} \cdot dT$; $\Delta C_{P_{II}}$ is the same as ΔC_{P_I} except that $C_p \cdot Zn(s)$ is replaced by $C_p \cdot Zn(l)$

$$\therefore \Delta C_p = -6.36 - 5.27 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}$$

$$\therefore \int_{693}^{1180} \Delta C_{P_{II}} \cdot dT = \int_{693}^{1180} (-6.36 - 5.27 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}) \, dT$$

$$= \left[-6.56T - 2.64 \times 10^{-3} T^2 - 17.45 \times 10^{5} T^{-1} \right]_{693}^{1150}$$

$$= -4460 \text{ J}$$

(x) To calculate $\int_{1150}^{1373} \Delta C_{p,III} \cdot dT$

$\Delta C_{p\,III}$ is the same as $\Delta C_{p\,II}$ except that $C_p, Zn(l)$ is replaced by $C_p \cdot Zn(g)$

$$\Delta C_{p\,III} = -16.45 - 5.27 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}$$

$$\therefore \int_{1150}^{1373} \Delta C_{p\,III} \cdot dT = \int_{1150}^{1373} (-16.45 - 5.27 \times 10^{-3} T + 17.45 \times 10^{5} T^{-2}) \, dT$$

$$= \left[-16.45T - 2.64 \times 10^{-3} T^2 - 17.45 \times 10^{5} T^{-1} \right]_{1150}^{1373}$$

$$= [-29,510] - [-25,160]$$

$$= -4350 \text{ J}$$

$$\Delta H_{1373} - \Delta H_{298} = \int_{298}^{693} \Delta C_{p\,I} \, dT + L_f(Zn) + \int_{693}^{1150} \Delta C_{p\,II} \, dT + L_e(Zn) + \int_{1150}^{1373} \Delta C_{p\,III} \, dT$$

Therefore

$$\Delta H_{1373} - (+237,700) = (-1500) + (+7280) + (-4460) + (+114,200) + (-4350)$$

and

$$\Delta H_{1373} = 237,700 + 110,900$$

$$= 348,600 \text{ J}$$

Hess's Law of Constant Heat Summation: which states that the overall heat change for a chemical reaction is the same whether it takes place in one or several stages, provided the temperature and either the pressure or the volume remain constant.

Ex: Calculate the heat of formation of solid lead oxide (PbO_2) from the reaction of solid lead and oxygen gas under 1 atm pressure if you given the following information at room temperature.

$$Pb_{(s)} + \frac{1}{2} O_2 \rightleftharpoons PbO_{(s)} \qquad \Delta H = -52.4 \text{ Kcal}$$

$$3PbO_{(s)} + \frac{1}{2} O_{2(g)} \rightleftharpoons Pb_3O_{4(s)} \qquad \Delta H = -18.4 \text{ Kcal}$$

$$Pb_3O_{4(s)} + O_{2(g)} \rightleftharpoons 3PbO_{2(s)} \qquad \Delta H = -22.7 \text{ Kcal}$$

Ans: $Pb_{(s)} + O_{2(g)} \rightleftharpoons PbO_{2(s)}$

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$$Pb_{(s)} + \frac{1}{2} O_2 \rightleftharpoons PbO_{(s)} \qquad \Delta H_{1} = -52.4 \text{ Kcal}$$

$$\frac{1}{3} \times 3PbO_{(s)} + \frac{1}{3} \times \frac{1}{2} O_{2(g)} \rightleftharpoons \frac{1}{3} Pb_3O_{4(s)} \qquad \Delta H_{2} = \frac{1}{3} \times -18.4 = -6.1 \text{ Kcal}$$

$$\frac{1}{3} \times Pb_3O_{4(s)} + \frac{1}{3} O_{2(g)} \rightleftharpoons \frac{1}{3} \times 3PbO_{2(s)} \qquad \Delta H_{3} = \frac{1}{3} \times -22.7 \text{ Kcal} = -7.6 \text{ Kcal}$$

$$Pb_{(s)} + O_{2(g)} \rightleftharpoons PbO_{2(s)} \qquad \Delta H = \Delta H_1 + \frac{1}{3}\Delta H_2 + \frac{1}{3}\Delta H_3$$

$$\Delta H = -52.4 - 6.1 - 7.6 = -66.1 \text{ Kcal}$$

Ex calculate the heat of formation of solid (WO_3) from the reaction of solid W and oxygen gas under 1 atm pressure and 25 C° . if you given the following information at 1atm pressure and room temperature .

$$W_{(s)} + O_{2(g)} \rightleftharpoons WO_{2(s)} \qquad \Delta H_{298} = -134 \text{ Kcal.}$$

$$3WO_{2(s)} + O_{2(g)} \rightleftharpoons W_3O_{8(s)} \qquad \Delta_{298} = -131.5 \text{ Kcal.}$$

$$W_3O_{8(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 3WO_{3(s)} \qquad \Delta_{298} = -66.5 \text{ Kcal}$$

Ans

$$W_{(s)} + \frac{9}{2}O_{2(g)} \rightleftharpoons 3WO_{3(s)}$$

$$3W_{(s)} + 3O_{2(g)} \rightleftharpoons 3WO_{2(s)} \qquad \Delta H_{298} \ (-134 \times 3) \text{ Kcal}$$

$$3WO_{2(s)} + O_{2(g)} \rightleftharpoons W_3O_{8(s)} \qquad \Delta H_{298} \ (-131.5) \text{ Kcal.}$$

$$W_3O_{8(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons 3WO_{3(s)} \qquad \Delta H_{298} \ (-66.5 \text{ Kcal})$$

$$3W_{(s)} + \frac{9}{2}O_2 = 3WO_3$$

$$\Delta H_{298} = (-134 \times 3) + (-131.5) + (-66.5)$$

Ea kcal/mol [illegible]

$$\Delta H_{298} = -200.0 \text{ Kcal.}$$