Contents

Key words: thermo chemistry, Heat of formation, Heat of reaction, Kirchoff's law

Preamble

All chemical processes involve various kinds of energy interchanges with the surrounding. Heat energy is the principal form of energy exchange between metallurgical systems and its surrounding in various extraction and refining of metals.

Thermo chemical calculations are required to perform energy balance of a process. Thermo chemical calculations are concerned with chemical changes that are accompanied by liberation or absorption of heat; for example

$$2Fe + 1.5O_2 = Fe_2O_3 \text{ and } C + O_2 = CO_2$$
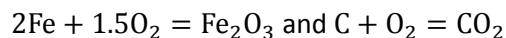
The formation of Fe_2O_3 is accompanied by evolution of 196.5×10^3 kcal of heat per kg mole of Fe_2O_3. Similarly $94.0.5 \times 10^3$ kcal of heat per kg mole is evolved when carbon on combustion produces CO_2. This lecture deals with basics of calculation of heat evolved or absorbed during a chemical reaction. Suitable examples are given to illustrate the basics of calculations.

First law of thermodynamics:

In the following, only a brief account is given. The first law equation for a process occurring is a systems is

$$\Delta E = E_2 - E_1 = Q - W$$

E_1 and E_2 are energy contents (internal energies) of the system in state 1 and state 2 (it must be clearly understood that thermodynamics deals with initial and final states), Q is the heat absorbed by the system from the surrounding and W is work done by the systems on the surrounding. Since E_2 and E_1 depend only on final and initial state of a systems, change in energy ΔE is independent of the path.

Since ΔE is independent of the path, $(Q - W)$ is also independent of path. However Q and W represent energy exchange with the surrounding and are not thermodynamic properties of the system. For

example, if for a given change in state by a path, heat Q absorbed is more than that path will also correspond to more work, W.

Some of the paths treated in thermodynamics are constant pressure, econstant volume, adiabatic (Q=0) and reversible ones. Extraction of metals is mostly carried at 1 atmospheric pressure. For constant pressure processes, more useful form of first law can be derived.

The heat content or enthalpy of systems (H) is a thermodynamic property

$$H = E + PV \qquad (2)$$

P is pressure and V is volume of the system. With the help of equation 1, first law is written for any thermodynamic change of state:

$$H_2 - H_1 = Q - W + P_2 V_2 - P_1 V_1 \qquad (3)$$

For a constant pressure process, only expansion work is done by system on surrounding and is equal to

$$\text{Expansion work} = \int_1^2 p \, dV \text{ also } P_2 = P_1 = p \qquad (4)$$

$$W = P(V_2 - V_1) \qquad (5)$$

By 3,4 and 5 we get

$$H_2 - H_1 = Q_p \text{ or } \Delta H = Q_P \qquad (6)$$

In equation Q_P is heat absorbed by system in changing from state 1 to state 2 by a path of constant pressure. A change under constant pressure is 1 called "ISOBARIC process".

If an isobaric processes involves work other than expansion

$$\Delta H = Q_P - W^1 \qquad (7)$$

W^1 does not include expansion work. For example in an electric process at constant pressure $-W^1$ is input of electrical work to the system.

The equation 6 is very useful since Q_P is related to the heat content (H). The change in heat content ΔH depends on the initial and final states only; hence heat absorption or evolution can be evaluated form the data on the properties of system in the two states.

Various heat effects

   a) Effect of temperature

The variation of heat content in pure compounds with temperature can be determined by

$$H_T - H_{298} = aT + bT^2 + cT^{-1} + d \qquad (8)$$

$H_T - H_{298}$ is increase in heat content in cal/mole as the substance is heated from 298K to T. In all calculations the reference temperature is 298K(25°C or 77°F). T is temperature in K and a, b, c and d are constants and depends on state or aggregation of the system. The quantity $H_T - H_{298}$ is called sensible heat,

Molal heat capacity at constant pressure is

$$C_p = a + 2bT - CT^{-2} \qquad\qquad (9)$$

$$C_p = \left(\frac{\partial H}{\partial t}\right)_P \therefore H_2 - H_1 = \int_{T_1}^{T_2} C_p \, dT \qquad (10)$$

Also change in heat content can be determined by mean heat capacity C_m

$$H_2 - H_1 = C_m(T_2 - T_1) \qquad\qquad (11)$$

$$C_m = \frac{\int_{T_1}^{T_2} C_p dT}{T_2 - T_1} \qquad\qquad (12)$$

We may write

$$H_2^1 - H_1^1 = C_m(T_2 - T_1) \qquad\qquad (13)$$

Equation 13 may be used to calculate heat content for rapid calculations. More accurate would be to use equation 8 or equations 9 and 10.

b) Changes in state of aggregation

When solid is heated to melting point additional heat must be supplied to melt it. At the melting print, this additional heat does not increase the temperature. The heat content for melting at constant pressure is called latent heat of fusion (ΔH_{fusion}) and this heat must be supplied at the melting point to transform solid into liquid. An equal quantity of heat is liberated during solidification so that

$$(\Delta H_{solidification}) = -(\Delta H_{fusion}) \qquad\qquad (14)$$

Negative sign indicates liberation of heat. Similarly, heat effects accompanying evaporation and allotropic changes in solids are measured by latent heat of vaporization and heats of transformation.

Value of ΔH for changes in state of aggregation vary with temperature and pressure under which change is carried out. For example heat of vaporization of water at 100°C is 542cal/g, whereas it is 583 cal/g at25°C.

Example The melting point of Cu is 1357K.

For solid Cu: $H_T - H_{298} = 5.41T + 0.75 \times 10^{-3} T^2 - 1680$

$$= 7042 \text{ cal/mol at melting point}$$

For liquid Cu $H_T - H_{298} = 7.50T - 20$

$$= 10158 \text{ cal/mol at melting point}$$

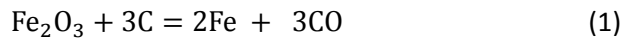Therefore $\Delta H_{fusion} = 10158 - 7042 = 3116 \text{cal/mol}$

c) Heat of formation

The formation of chemical compound from its elements is associated with either absorption or liberation of heat. Thus the formation of $H_2O(l)$ form the elements at 298K (25°C) can be written
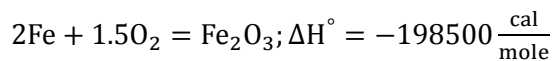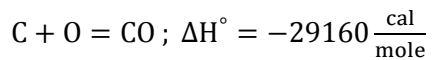
$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$
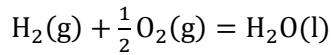
$\Delta H_{298}^0 = -68320$ cal/mol at 1 atm pressure

d) Heat of reaction

ΔH for any process depends only on the initial and final states and not on the path. If a process is divided into several steps, and ΔH is determined for each step, the algebraic sum of the ΔH values of all steps will be equal to ΔH for the original process. Consider an example to calculate heat of reaction of the following reaction:

$$Fe_2O_3 + 3C = 2Fe + 3CO \qquad\qquad (1)$$

This reaction comprises of the following reactions:

$$C + O = CO\,; \ \Delta H^\circ = -29160\,\frac{cal}{mole}$$

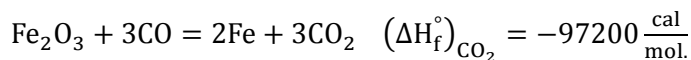$$2Fe + 1.5O_2 = Fe_2O_3; \Delta H^\circ = -198500\,\frac{cal}{mole}$$

Heat of formation for reaction 1 at 298K is

$$\left(\Delta H_f^\circ\right)_{298} = 3\,\Delta H_{CO}^\circ - \Delta H_{Fe_2O_3}^\circ \qquad\qquad (2)$$

It must be noted that heat of formation of element is zero by using the value of ΔH° we get

$\left(\Delta H_f^\circ\right)_{298} = 111020$ cal/mol Fe_2O_3(endothermic), that means reaction 1 is accompanied by absorption of heat.

Consider the reaction

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \quad \left(\Delta H_f^\circ\right)_{CO_2} = -97200\,\frac{cal}{mol.}$$

$$\left(\Delta H_f^\circ\right)_{298} = 3 \times \left(\Delta H_f^\circ\right)_{CO_2} - \left(\Delta H_f^\circ\right)_{Fe_2O_3} - 3\left(\Delta H_f^\circ\right)CO$$

$$= -5620 \text{ cal/mol } Fe_2O_3. \text{ This is exothermic reaction.}$$

The heat of reaction calculated above are at 298K (25°C). Heat of reaction depends on temperature and can be determined

$$\left(\Delta H_f^\circ\right)_{T_2} = (\Delta H_f)_{298} + \Sigma(H_{T2} - H_{298})_{products} - \Sigma\left(H_{T_2} - H_{T_1}\right)_{reactants} \qquad 15)$$

Conclusion

This lecture discusses the basics of thermo chemistry as required to calculate the different types of heat associated with a chemical reaction. Heat of formation, latent heat of fusion, evaporation and transformation are discussed and illustrated with a suitable example. Effect of temperature on heat of reaction is also given. For details the readers may go through the references.

References:

Schuhmann: Metallurgical Engineering Principles

Alan and Geiger: energy balance in metallurgical processes