

## THERMODYNAMICS AND THERMOCHEMISTRY

### System and Surroundings

The substance or mixture of substances under study in which a change occurs is called the thermodynamic system (or simply system). The *surroundings* are everything in the vicinity of the thermodynamic system. Thus a portion of the universe which is under investigation is called *system* and everything else in the universe except system is called surroundings.

Because energy can neither be created nor destroyed, any gain or loss of energy by a system must be accompanied by an equivalent loss or gain of energy in the surroundings. The change in energy content of a system is often determined by measuring the energy gained by or withdrawn from the surroundings.

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A system may be as complex as a human body or as simple as a mixture consisting of a drop of acid and a drop of base. We can regard the surroundings either as a source of energy to put into our system or as a sink into which we can dump energy from the system.

1. System can be *open* if it can exchange heat and matter with surroundings.
2. System can be *closed* if it can exchange heat but not the matter with surroundings.
3. System can be *isolated* if it can exchange neither heat nor matter with surroundings.

A system is said to be macroscopic when it consists of a large number of molecules, atoms or ions. Properties associated with a macroscopic system are called macroscopic properties; pressure, volume, temperature, mass, composition, surface area etc. are macroscopic properties.

A system is homogeneous when it is completely uniform throughout—a system with one phase, pure gas, pure liquid or pure solid. A system is heterogeneous when it is not uniform throughout—a system with two or more phases.

### Thermodynamic equilibrium

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamic equilibrium.

If there is no flow of heat from one portion of the system to another then system is said to be in thermal equilibrium. This is only possible if temperature remains constant throughout in all parts of the system.

If no mechanical work is done by one part of the system on another part of the system then system is said to be in mechanical equilibrium. This is only possible if pressure remains same throughout in all parts of the system.

If composition of the various phases in the system remains the same throughout then system is said to be in chemical equilibrium.

### Process

The operation by which a system changes from one state to another is called a **process**. A process is accompanied by change in energy (and matters also if system is open).

1. If a process is taking place at constant temperature, it is said to be isothermal (iso-same, therm-heat, temperature) process.
2. If a process is taking place at constant pressure, it is said to be isobaric process.
3. If a process is taking place at constant volume, it is said to be isochoric process.
4. If no heat enters or leaves the system during any step of the process, it is said to be adiabatic process.

### First Law of Thermodynamics

Energy can neither be created nor destroyed, although it can be transformed from one form to another. This is also called as the law of conservation of energy.

Mathematically,

$$\Delta E = q + W$$
$$\Delta E = q - P \Delta V$$

Where,  $W$  is the work done on the system,  $q$  the heat transferred to it and  $\Delta E$  the change in internal energy. Again note that in SI convention  $W$  has positive sign.

In non-SI convention above equation is written as

$$\Delta E = q - W$$

When  $W$  or  $q$  is positive, it means that energy has been supplied to the system as work or as heat. The internal energy of the system in such cases increases.

When  $W$  or  $q$  is negative, it means that energy has been lost by the system as work or as heat. The internal energy of the system in such a case decreases.

### Enthalpy Change

Generally, the amount of heat,  $q$  that a system absorbs or evolves as it changes is not state function; it varies with the method the process has adopted. If the change occurs in such a way that the only work done is to affect a change in volume of the system at constant pressure, then  $q$  reflects a change in a state function of the system called enthalpy,  $H$  defined by equation.

$$H = E + P \Delta V$$

### Second Law of Thermodynamics

The second law of thermodynamics is a general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines.

#### Entropy

The direction of a spontaneous process for which the energy is constant is always the one that increase the molecular disorder or randomness. The thermodynamic property that measures the amount of molecular disorder is called the entropy, denoted by  $S$ .

#### Entropy and the Second Law of Thermodynamics

In terms of entropy second law of thermodynamics is defined as, 'entropy of the system and surrounding remains constant in a reversible equilibrium process, while it increases in an irreversible process'.

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$$

In nature, all the processes are irreversible (spontaneous) going to completion; hence, entropy of the universe increases and tends to be maximum.

Work done in a reversible process is always maximum;

Hence,

$$q_{\text{reversible}} > q_{\text{irreversible}}$$

Or,

$$\frac{q_{\text{reversible}}}{T} > \frac{q_{\text{irreversible}}}{T}$$

$$\left( \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irrev}}}{T} \right) > 0$$

$$\Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$$

Specifically:

- If  $S_{\text{Total}} > 0$ , the reaction is spontaneous
- If  $S_{\text{Total}} < 0$ , the reaction is nonspontaneous
- If  $S_{\text{Total}} = 0$ , the reaction mixture is at equilibrium

Also for an endothermic reaction, system gains heat hence entropy  $\Delta S = \frac{\Delta H}{T}$  of the system increases;

For an endothermic reaction;  $\Delta S_{\text{System}} > 0$  and  $\Delta S_{\text{Surrounding}} < 0$

For an exothermic reaction;  $\Delta S_{\text{System}} < 0$  and  $\Delta S_{\text{Surrounding}} > 0$

### Free Energies

Gibbs free energy  $G$  is defined as;

$$G = H - TS$$

Where,  $H$  is the enthalpy,  $T$  is the temperature in Kelvin scale,  $S$  is the entropy.  $TS$  is the part of system's energy that is already disordered and  $H-TS (= G)$  is the part of system's energy and that is still ordered hence free (available) to cause spontaneous change by becoming disordered.

$G$  is also a state function hence change in free energy ( $\Delta G$ ) for process is independent of path.

$$\Delta G = \Delta H - T\Delta S$$

Also,

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$$

$$\Delta G = \Delta S - \frac{\Delta H}{T}$$

$$T\Delta S_{\text{Total}} = T\Delta S - \Delta H$$

$$-T\Delta S_{\text{Total}} = \Delta H - T\Delta S$$

$$T\Delta S_{\text{Total}} = \Delta G$$

Thus,  $\Delta G$  and  $\Delta S_{\text{Total}}$  have opposite signs ( $T$  is always positive); hence sign of  $\Delta G$  can also be used to predict feasibility of a reaction at constant temperature and pressure.

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
- ] Exothermic	+	-	Spontaneous at all temperatures
	-	-	Spontaneous at low temperatures
		+	Non-spontaneous at high temperatures
+ ] Endothermic	+	+	Non-spontaneous at low temperatures
	+	-	Spontaneous at high temperatures
	-	+	Non-spontaneous at all temperatures
$T\Delta S = \Delta H$		0	Equilibrium

For a reaction to be:

1. Spontaneous if  $\Delta S > 0$  then  $\Delta G < 0$
2. Nonspontaneous if  $\Delta S < 0$  then  $\Delta G > 0$
3. In equilibrium if  $\Delta S = 0$  then  $\Delta G = 0$

Thus, decrease in G, ( $-\Delta G$ ) is equal to net work done = total work - mechanism work.

Free Energy and Electromotive Force (E.M.F) of a Cell

Using,

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

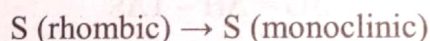
We have

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + 2.303 RT \log Q$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q$$

This is called Nernst equation for e.m.f of a cell.  $E_{\text{cell}}$  is the e.m.f of a cell in a given state,  $E_{\text{cell}}^\circ$  is the standard e.m.f., 'n' the number of electrons exchanged, F the Faraday of electricity, R gas constant and T the temperature.

**Example 13:** Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs.



If  $\Delta H = 276.144 \text{ J}$  at 298 K and 1 atm and  $\Delta G = 75.312 \text{ J}$ . a) calculate  $\Delta S$  at 298 K and, b) assume that  $\Delta H$  and  $\Delta S$  do not vary significantly with temperature, calculate  $T_{\text{eq}}$ , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

**Solution:**

(a) Since,  $\Delta G = \Delta H - T\Delta S$

$$\therefore \Delta S = \frac{\Delta H - \Delta G}{T}$$
$$= \frac{276.144 - 75.312}{298}$$

$$= 0.674 \text{ JK}^{-1}$$

(b) Under equilibrium condition,  $\Delta G = 0$

$$\therefore \Delta H - T_{\text{eq}}\Delta S = 0$$

$$\therefore T_{\text{eq}} = \frac{\Delta H}{\Delta S} = \frac{276.144}{0.674}$$
$$= 409.7 \text{ K}$$

**Example 14:** In the Daniell cell, the reaction  $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightleftharpoons \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$  occurs spontaneously, and the cell delivers 1.10 volt when all substances are at 1M concentration at 298 K. Calculate  $\Delta G^\circ$  and equilibrium constant k.

**Solution:**

Using,

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96500 \times 1.1 \text{ J}$$

$$= -2.123 \times 10^5 \text{ J}$$

also,

$$E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log k$$

$$1.10 = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log k$$

$$\log k = 37.2074$$

$$k = 1.61 \times 10^{37}$$