15.15 Entropy

The original statement of the second law of thermodynamics is concerned with the development of the theoretical aspect of heat engine, specially the Carnot's cycles. This has little implication in the chemical processes.

For a chemist, attempts were made to answer the question of feasibility of a reaction. As is known that a state with minimum energy is the most stable state of a system, therefore, in this universe there is a natural tendency of all systems to stabilise by acquiring minimum energy. It was believed that all processes in which energy decreases (exothermic, having negative value of ΔH) occur spontaneously. Hence, decrease in enthalpy is the driving force behind the spontaneous processes. However, there are many endothermic reactions (ΔH positive) that are spontaneous. For example,

- Water absorbs energy and is evaporated (endothermic process) but it is spontaneous in nature.

  $H_2O\ (l) \rightarrow H_2O\ (g) \qquad\qquad \Delta H = +\ 44.0\ kJ\ mol^{-1}$
- Melting of ice is endothermic but spontaneous.
- A crystal of potassium permanganate dropped in a beaker spontaneously diffuses in water without any perceptible change in the heat content.
- Salts like ammonium nitrate dissolve spontaneously by absorption of heat.

How are these processes spontaneous? It is definite that this cannot be explained by considering the decrease in enthalpy alone. There are some additional contributory factors to the spontaneity of these reactions; it is this search for another factor that has resulted in describing another property of the system called **entropy**.

Entropy and its physical significance

To explain this term let us consider a process that does not involve energy changes or is endothermic.

Mixing of two gases Let us consider a box having two partitions, each having a different gas. When this partition is lifted, the diffusion of gases occurs and they get mixed up. We can also say that the gas molecules now have a larger space for their movement. In statistical language, we can say that the probability of finding a molecule at a particular place or point has decreased or the chaos has increased.

Conversion of solids into liquids When a solid melts into a liquid ($\Delta H = +$ ve), the particles have more freedom to move in the liquid state. Similarly, ammonium nitrate dissolves in water, the solid particles leave their lattice position and move about freely in the dissolved state. Hence, we can say that the randomness or disorder increases.

Entropy is a property that is used to express this extent of disorder or randomness of a system and may be defined as the thermodynamic property that is a measure of the randomness or disorder of the molecules of a system.

Mathematical formulation of entropy

The concept of entropy was first introduced in connection with the theory of heat engines and it is more important for engineers. It was only later that chemists could make use of it in chemical processes.

Entropy is expressed by the symbol 'S'. Like internal energy and enthalpy, entropy is also a state function and therefore change in entropy depends only on the initial and final states of the system.

Change in entropy is given by

$\Delta S = S\ (\text{final state}) - S\ (\text{initial state})$.

For a reversible process at equilibrium, the change in entropy is expressed as

$$dS = \frac{dq_{rev}}{T}$$

Thus, entropy change may be defined as the amount of heat absorbed by the system in a reversible manner divided by the absolute temperature at which the heat is absorbed.

Units of entropy

As entropy change is expressed as heat divided by temperature, the units of entropy are calories per degree (expressed as entropy unit eu, 1 eu = 1cal deg^{-1}) or Joule per Kelvin (J K^{-1}). (For 1 mole of a substance the units of entropy are cal $deg^{-1}mol^{-1}$. This is called molar entropy)

15.16 Second Law of Thermodynamics in Terms of Entropy

If gases are mixed in an isolated system, then there is no exchange of energy or matter between the system and the surroundings. The process occurs because the randomness or entropy increases. Hence, for a spontaneous process in an isolated system, entropy change is positive, that is, $\Delta S > 0$. However, if the system is not isolated, the entropy changes of both the system and surroundings have to be taken into account. Then, the sum of entropy changes of the system (ΔS_{system}) and the surrounding ($\Delta S_{surroundings}$) gives the total entropy change (ΔS_{total}).

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

For a spontaneous process, ΔS_{total} must be positive, that is,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0.$$

The system and the surroundings together constitute the universe. Therefore, for a spontaneous change,

$$\Delta S_{universe} > 0.$$

Hence, according to the second law of thermodynamics '*in any natural process the energy of the universe is conserved but the entropy of the universe always increases*'.

Entropy is a state function

In the definition of entropy, the quantity q_{rev} is not a state function and depends on the path of the reaction, whereas the $\frac{dq_{rev}}{T}$ is a perfect differential. This can be shown as follows:

Suppose 1 mole of an ideal gas is undergoing a reversible expansion. From the first law,

$$dq_{rev} = dE - dw$$

For work expansion $-dw = PdV$ hence,

$$dq_{rev} = dE + PdV \quad (1) \qquad (\because PV = RT \quad , \; P = \frac{RT}{V} \; \text{similarly} \; C_v = \left(\frac{\partial E}{\partial T}\right)_V$$

$$\text{or} \quad dE = C_v dT \;)$$

$$= \quad C_V dT + \frac{RT}{V} dV$$

$$\text{or} \quad dq_{rev} = \int C_V dT + \int \frac{RT}{V} dV \qquad (2)$$

As dq_{rev} is not an exact differential, it cannot be integrated. This is confirmed by observing the right hand side of Eq. (2) where $\int \frac{RT}{V} dV$ cannot be evaluated unless we specify the path or in other words the relation between T and V is known. The value of V will be different for different values of T. Thus, dq_{rev} depends on the path by which the gas is expanded. Dividing Eq. (2) by T on both sides we get

$$\int \frac{dq_{rev}}{T} = \int \frac{C_V dT}{T} + \int \frac{RT}{V} \frac{1}{T} dV$$

$$= \int \frac{C_V dT}{T} + \int \frac{R}{V} dV$$

$$= C_V \ln T + R \ln V + \text{constant}$$

It follows that $\int \frac{dq_{rev}}{T}$ can be evaluated; hence, $\frac{dq_{rev}}{T}$ is an exact differential. Hence, we may conclude that entropy change dS is a perfect differential and hence entropy S is a state function.

Thus, if a system changes from the initial state 1 to the final state 2, the entropy change is expressed by integrating the equation $S = \frac{dq_{rev}}{T}$ between the limits of the initial state 1 and final state 2.

$$\int_1^2 dS = \int_1^2 \frac{dq_{rev}}{T}$$

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$$

where S_1 and S_2 are the entropies of the system in initial and final states respectively.

It must be born in mind that entropy change dS is equal to the amount of heat absorbed divided by the absolute temperature only when the process is carried out reversibly.

15.17 Evaluation of Entropy

1. **Entropy changes for an ideal gas**

Consider a system consisting of *n* moles of an ideal gas occupying a volume V at a pressure P and temperature T. If dq_{rev} amount of heat is absorbed by the system reversibly, then the increase in entropy of the system dS is given by

$$dS = \frac{dq_{rev}}{T} \qquad (1)$$

From the first law of thermodynamics, for a reversible process in which only pressure – volume work is involved

$$dq_{rev} = dE - dw$$

For work expansion there is infinitesimal increase in volume dV against pressure P, hence

$$-dw = PdV$$

$$\therefore\ dq_{rev} = dE + PdV \qquad (2)$$

Substituting the value of dq_{rev} in Eq. (1) we get

$$dS = \frac{dE + PdV}{T} \qquad (3)$$

For *n* moles of an ideal gas, we know that

$$PV = nRT \quad \text{and} \quad dE = nC_V dT$$

where C_V is the molar heat at constant volume.
Substituting these values in Eq. (3) we get,

$$dS = \frac{nC_V dT + \frac{nRT}{V} dV}{T}$$

$$\text{or} \qquad \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V} \qquad (4)$$

If the entropy, volume and temperature of the system in the initial state are S_1,V_1 and T_1 and in the final state are S_2, V_2 and T_2 respectively, then integrating Eq. (4) between these limits we get

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

Assuming C_V to be independent of temperature over the temperature range considered, we obtain

$$\Delta S = S_2 - S_1 = nC_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1} \quad ....(5) \qquad (5)$$

For 1 mole of an ideal gas,

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \quad ....(6) \tag{6}$$

An alternate form of Eq. (5) involving pressure terms can be obtained in the following manner If P_1 is the pressure of the system in the initial state and P_2 in the final state, then from the gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

or $$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

Substituting in Eq. (5) we obtain,

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{P_1T_2}{P_2T_1}$$

$$\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$= n(C_V + R)\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

Since $(C_V + R) = C_P$ Hence

$$\Delta S = nC_P \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} \tag{7}$$

From Eqs (5), (6) and (7), entropy change for an ideal gas can be calculated. These equations take different forms under different conditions.

(i) **For isothermal process** When $T_1 = T_2$ then Eqs (5) and (7) are reduced to

$$\Delta S_T = nR\ln\frac{V_2}{V_1} \quad ......(8) \tag{8}$$

and $$\Delta S_T = nR\ln\frac{P_1}{P_2} \quad .....(9) \tag{9}$$

The subscript T in ΔS_T indicates that the process is occurring at constant temperature. In the expansion process $V_2 > V_1$ or $P_1 > P_2$., ΔS_T is positive but in contraction $V_2 < V_1$ or $P_1 < P_2$ and hence ΔS_T is negative. From this, it is concluded that in an isothermal expansion entropy increases and in contraction it decreases.

(ii) **For an isobaric process** When $P_1 = P_2$, Eq. (7) reduces to

$$\Delta S_P = nC_P \ln\frac{T_2}{T_1} \tag{10}$$

(iii) **For an isochoric process** When $V_1 = V_2$, then Eq. (6) reduces to

$$\Delta S_V = nC_V \ln\frac{T_2}{T_1} \tag{11}$$

Solved examples

1. Calculate the change in entropy accompanying the isothermal expansion of 5 moles of an ideal gas at 330 K until its volume has increased six times.

Solution

Entropy change during isothermal expansion of an ideal gas

$$(\Delta S)_T = 2.303nR\log\frac{V_2}{V_1} = 2.303\times5\times8.314\ \text{J K}^{-1}\text{mol}^{-1}\log\frac{6}{1}$$
$$= 2.303\times5\times8.314\times0.7782 = 74.5\ \text{J K}^{-1}$$

2. Calculate the entropy change involved in expanding 1 mole of an ideal gas from 15 L at 2 atm pressure to 50 L at 1 atm pressure.($C_P = 7.42$ cal deg^{-1} mol^{-1})

Solution

$$\Delta S = nC_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} = 2.303nC_p\log_{10}\frac{T_2}{T_1} + 2.303\ nR\ \log_{10}\frac{P_1}{P_2}$$

$n = 1\,\text{mole};\quad C_P = 7.42\,\text{cal}\,\text{deg}^{-1}\ \text{mol}^{-1}$

$R = 1.987\ \text{cal deg}^{-1}\ \text{mol}^{-1}\ ;\ P_1 = 2\ \text{atm}\ ;\ P_2 = 1\ \text{atm}$

For an ideal gas $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

or $\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{50\times1}{15\times2} = \frac{5}{3}$

$$\therefore \Delta S = 2.303\times1\times7.4\ \log_{10}\frac{5}{3} + 2.303\times1\times1.987\ \log_{10}\frac{2}{1}$$

$$= 3.779 + 1.377 = 5.156\ \text{cal deg}^{-1}$$

3. Calculate the entropy change when 3 moles of an ideal gas (C_v = 7.88 cal deg^{-1} mol^{-1}) are heated from a volume of 200 L at 50 °C to a volume of 300 L at 150 °C.

Solution

$$\Delta S = 2.303\ nC_V\ \log_{10}\frac{T_2}{T_1} + 2.303\ nR\ \log_{10}\frac{V_2}{V_1}$$

Here, $n = 3$ mole, $C_V = 7.88 \text{ cal deg}^{-1} \text{ mol}^{-1}$ $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$

$T_1 = 273 + 50 = 323$ K; $T_2 = 273 + 150 = 423$ K; $V_1 = 200$ L; $V_2 = 300$ L.

$$\Delta S = 2.303 \times 3 \times 7.88 \log_{10} \frac{423}{323} + 2.303 \times 3 \times 1.987 \times \log_{10} \frac{300}{200}$$
$$= 6.377 + 2.417 = 8.794 \text{ cal deg}^{-1}$$

4. Calculate the entropy change when 1 mole of an ideal gas is heated from 20 °C to 40 °C at a constant pressure. The molar heat at constant pressure of the gas over this temperature range is 6.189 cal deg^{-1}.

Solution

For an isobaric process,

$$\Delta S_P = 2.303 \; nC_P \; \log_{10} \frac{T_2}{T_1}$$

Here

$n = 1 \text{ mole} \;\; ; \;\; C_P = 6.189 \text{ cal deg}^{-1}$

$T_1 = 273 + 20 = 293 \text{ K} \;\; ; \;\; T_2 = 273 + 40 = 313 \text{ K}$

$$\Delta S_P = 2.303 \times 1 \times 6.189 \times \log_{10} \frac{313}{293}$$
$$= 0.4087 \text{ cal deg}^{-1}$$

Practice problems

1. 1 mole of an ideal gas ($C_V = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$) is transferred from 298 K and 2 atm to 233 K and 0.4 atm. Calculate the value of entropy change in the system.

[Ans 10.294 J K^{-1} mol^{-1}]

2. 1 mole of an ideal gas ($C_V = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$) is heated from 300 to 600 K. Calculate entropy change when (a) volume is kept constant, (b) pressure is kept constant.

[Ans (a) 8.645 J K^{-1} mol^{-1} (b) 14.408 J K^{-1} mol^{-1}]

3. Calculate the entropy change when 5 moles of an ideal gas undergoes isothermal expansion at 20 °C from a pressure of 10 atm to a pressure of 2 atm. [Ans 66.909 J deg^{-1}]

4. Calculate the entropy change when 2 mole of an ideal gas is allowed to expand from a volume of 1 L to a volume of 10 L at 27 °C. [Ans 38.294 J K^{-1}]

2. Entropy change in heating a solid or a liquid

When a solid or a liquid is heated without producing change in state, the heat change is given by

Quantity of heat absorbed = mass × specific heat × temperature rise.

= number of moles × molar heat × temperature rise.

Thus, if *m* g of a solid or a liquid of specific heat *s* is heated reversibly through temperature dT, the amount of heat absorbed is given by

$dq_{rev} = msdT$

∴ Entropy change $$dS = \frac{dq_{rev}}{T} = \frac{msdT}{T}$$

or $$\int \Delta S = \int_{T_1}^{T_2} \frac{msdT}{T} \tag{12}$$

Assuming that s remains constant within the temperature limits T_1 and T_2, Eq. (12) on integration gives,

$$\Delta S = ms \ln \frac{T_2}{T_1} = 2.303\ ms \log_{10} \frac{T_2}{T_1} \tag{13}$$

3. **Entropy change during phase transition** When matter changes from one phase to another like from the solid phase to the liquid phase or from liquid to gaseous phase, then it is termed as the phase transition. Melting of solid or vaporisation of liquid occurs at constant temperature as the two phases are in equilibrium at all times. The entropy change for these reactions may be calculated as

$$\Delta S_{trans} = \frac{q_{rev}}{T}$$

where q is the heat evolved or absorbed during transition and T is the temperature. For transformation of 1 mole of a substance at constant pressure, q_{rev} is equal to the molar enthalpy change for that transformation, that is, $q_{rev} = \Delta H_{trans}$. Let us consider some examples

(i) **Entropy of fusion** Entropy of fusion is the entropy change during the conversion of 1 mole of the solid substance into liquid form at its melting point. For example, when ice melts,

Water (s) $\rightleftharpoons$ Water (l)

The change in entropy is given by

$$S_{water} - S_{ice} = \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \tag{14}$$

where ΔH_{fusion} the enthalpy of fusion and T_f is the fusion temperature.

(ii) **Entropy of vaporisation** Entropy of vaporisation is the change in entropy when 1 mole of a liquid changes into vapor at its boiling point. The entropy of vaporisation of a liquid at its boiling point is

$$\Delta S_{vaporization} = \frac{\Delta H_{vap}}{T_b} \tag{15}$$

where ΔH_{vap} is the entropy of vaporisation and T_b is the boiling point.

Practice problems

1. Calculate the entropy change when 2 moles of lead is heated from 27 °C to 28 °C. The specific heat of lead over this temperature range is 0.03 cal g^{-1} and the atomic weight of lead is 207.

Solution

$$\Delta S = 2.303 \text{ ms } \log_{10} \frac{T_2}{T_1}$$

Here, m = 2 × 207 = 414 g ; s = 0.03 cal g^{-1} ; T_1 = 273 + 27 = 300 K ; T_2 = 273 + 28 = 301 K.

$$\Delta S = 2.303 \times 414 \times 0.03 \times \log_{10} \frac{301}{300}$$
$$= 0.0413 \text{ cal K}^{-1}$$

2. Calculate the molar entropy of vaporisation of 1 mole of water at 100 °C. Latent heat of vaporisation of water at 100 °C is 540 cal/g.

Solution

$$\Delta S = \frac{\Delta H_{vap}}{T_b} = \frac{540 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{373} = 26.059 \text{ cal mol}^{-1}\text{K}^{-1}$$

3. Calculate the total entropy change when 5 moles of ice at 0 °C and 1 atm is converted into steam at 100 °C. The molar heat of fusion of ice and molar heat of vaporisation of water are 1440 and 9720 cal mol^{-1}. The molar heat capacity of water over this temperature range may be taken equal to 18 cal mol^{-1}.

Solution

The process is irreversible. To compute the entropy change, the given process may be imagined to be carried out reversibly in the following three steps

(i) H_2O (s) at 0 °C → H_2O (l) at 0 °C.

(ii) H_2O (l) at 0 °C → H_2O (l) at 100 °C.

(iii) H_2O (l) at 100 °C → H_2O (g) at 100 °C.

The molar entropy change for process (i) is given by

$$\Delta S_1 = \frac{\Delta H_{fusion}}{T_f} = \frac{1440}{273} = 5.274 \text{ cal mol}^{-1}\text{K}^{-1}$$

The molar entropy change in process (ii) is given by

$$\Delta S_2 = 2.303 \, C_P \, \log_{10} \frac{T_2}{T_1}$$
$$= 2.303 \times 18 \times \log_{10} \frac{373}{273} = 5.616 \text{ cal mol}^{-1} \text{ K}^{-1}$$

The molar entropy change in process (iii) is given by

$$\Delta S_3 = \frac{\Delta H_{vap}}{T_b} = \frac{9720}{373} = 26.06\,\text{cal mol}^{-1}\text{K}^{-1}$$

∴ The total molar entropy change $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$= 5.274 + 5.616 + 26.06 \quad = 36.95$ cal K^{-1} mol^{-1}.

The total entropy change for 5 moles = 5 × 36.95 = 184.75 cal K^{-1}.

4. ΔS_{vap} of acetone is 93.0 J K^{-1} mol^{-1}. If the boiling point of acetone is 56 °C, calculate the heat required to vaporise 1 g of acetone.

Solution

$\Delta S_{vap} = 93.0$ J $K^{-1}mol^{-1}$; $T_b = 273 + 56 = 329$ K.

$$\Delta S_{vap} = \frac{\Delta H}{T_b}$$

$$\Delta H = \Delta S_{vap} \times T_b = 93 \times 329 = 30597 \text{ J mol}^{-1}$$

Heat required to vaporise 1 mole acetone = 58 g = 30597 J mol^{-1}

∴ Heat required to vaporise 1 g acetone = $\frac{30597}{58} = 527.5$ J

Practice problems

1. Determine the entropy of fusion of ice, if its latent heat of fusion is 6.025 kJ mol^{-1}.
[Ans = 22.07 J K^{-1} mol^{-1}]
2. Find the change in entropy when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 9522 cal mol^{-1}. [Ans = 27.128 cal K^{-1} mol^{-1}]
3. 30.4 kJ of heat is required to melt 1 mole of sodium chloride. The entropy change during melting is 28.4 J mol^{-1} K^{-1}. Calculate the melting point of sodium chloride.
[Ans = 1070.4 K]
4. If ΔS = 109.8 J K^{-1} mol^{-1} and boiling point of ethanol = 78.5 °C, find out the enthalpy of vaporisation per mole for ethanol [Ans 38.595 kJ mol-1]

15.18 Entropy Changes in a Reversible Process

Total entropy change of the universe can be evaluated by considering the entropy change of the system as well as that of the surroundings. When a system gains heat, the surrounding loses heat and hence their entropies also change. The total change in entropy will, therefore, be equal to the algebraic sum of the entropy change of the system and the surroundings, that is,

$$\Delta S = \Delta S_{system} + \Delta S_{surrounding}$$

If an ideal gas undergoes an isothermal reversible expansion and absorbs heat equal to q_{rev} at temperature T, then the entropy change of the gas, that is, system is given by

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

As the expansion is reversible, the system is in equilibrium with its surroundings at all times during the expansion. Hence, the surroundings lose an amount of heat equal to q_{rev} or we can say that the surrounding absorb (–) q_{rev} of heat. The entropy change of the surroundings is given by

$$\Delta S_{surroundings} = -\frac{q_{rev}}{T}$$

∴ the total entropy change of the universe,

$$\Delta S = \Delta S_{system} + \Delta S_{surroundings}$$

$$= \frac{q_{rev}}{T} - \frac{q_{rev}}{T}$$

$$\Delta S = 0 \tag{16}$$

Hence, it can be concluded that for a reversible process the total entropy change of the universe is zero.

However a thermodynamically irreversible process is always accompanied by an increase in entropy of the system and surroundings taken together .

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

15.19 Entropy Change in a Irreversible Process

In an irreversible or spontaneous process, the entropy of the universe increases. This can be illustrated by taking the following examples

(i) **Isothermal expansion of an ideal gas** Consider an irreversible isothermal expansion of an ideal gas. Suppose *n* moles of an ideal gas expands irreversibly from a volume V_1 to a volume V_2, as ΔS_{system} is independent of the path of the change it is given by

$$\Delta S_{system} = nR \ln \frac{V_2}{V_1}$$

The entropy change of the surroundings will, however, be different. Let us take the extreme case of isothermal free expansion, that is, expansion in vacuum. In this case no work is done by the gas, that is, w = 0. For an isothermal process, ΔE = 0. According to the first law of thermodynamics,

$$q = \Delta E - w.$$

$$= 0 + 0 = 0.$$

This shows that no heat is absorbed by the system and as such no heat will be given up by the surroundings and consequently

$$\Delta S_{\text{surroundings}} = 0$$

∴ the total entropy change of the universe-

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= nR \ln \frac{V_2}{V_1} + 0$$

or $\Delta S = nR \ln \frac{V_2}{V_1}$

As $V_2 > V_1$, the value of ΔS is positive; hence, in an irreversible expansion of an ideal gas the entropy of the universe increases.

German physicist Rudolf Clausius (1822–1888) summed up the first and second law stating that: the energy of the universe remains constant and the entropy of the universe tends towards a maximum.

15.20 Entropy of Mixing

When different gases are allowed to mix freely at constant temperature and pressure, there is an increase in entropy. On mixing, the molecules of each gas are free to move in a large volume, that is, their randomness increases and hence entropy increases.

Quantitative expression

Entropy change (dS) for 1 mole of an ideal gas is given by

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

Assuming C_v to be constant for an ideal gas and integrating this equation, we get

$$\int dS = C_V \int \frac{dT}{T} + R\int \frac{dV}{V}$$

$$S = C_V \ln T + R \ln V + S_0 \qquad \{S_0 = \text{integration constant}\} \qquad (17)$$

Now $V = \frac{RT}{P}$

Placing the value of V in Eq. (17), we have

$$S = C_V \ln T + R \ln T + R \ln R - R \ln P + S_0$$

$$S = C_P \ln T - R \ln P + S_0' \qquad (\because C_P = C_V + R)$$

where $S_0' = R \ln R + S_0$

Now, let us consider a gaseous mixture containing n_1, n_2, …, etc., moles of various gases and let their partial pressures be p_1, p_2 …, etc., respectively, then entropy of the mixture is

$$\begin{aligned} S &= n_1(C_P \ln T - R\ln p_1 + S_0^{/}) + n_2(C_P \ln T - R\ln p_2 + S_0^{/}) + \ldots\ldots\ldots. \\ &= \sum n(C_P \ln T - R\ln p + S_0^{/}) \end{aligned}$$

Now partial presure (p) = Mole fraction(X) $\times$ Total pressure P

$$\therefore S = \sum n(C_P \ln T - R\ln P + R\ln X + S_0^{/})$$

Entropy change during mixing of ideal gases

Suppose n_1, n_2, …, etc., are the number of moles of ideal gas 1, 2, … etc., and V_1, V_2, … etc., are the volumes of the individual gas. Then, at constant temperature

$$\begin{aligned} \Delta S_{\text{mixing}} &= S_{\text{final}} - S_{\text{initial}} \\ &= \left[n_1 R\ln(V_1 + V_2 + \ldots..) - n_1 R\ln V_1\right] - \left[n_2 R\ln(V_1 + V_2 + \ldots..) - n_2 R\ln V_2\right] + \ldots\ldots \end{aligned}$$

$$= -n_1 R\ln\frac{V_1}{(V_1 + V_2 + \ldots..)} - n_2 R\ln\frac{V_2}{(V_1 + V_2 + \ldots..)}$$

$$\text{But}\quad \frac{V_1}{(V_1 + V_2 + \ldots..)} = \frac{n_1}{n_i} = X_1 \quad ; \frac{V_2}{(V_1 + V_2 + \ldots..)} = \frac{n_2}{n_i} = X_2$$

where n_i is the total number of moles in the gases in the system and X gives the mole fraction of the individual gases.

$$\begin{aligned} \therefore \Delta S_{\text{mixing}} &= -R\left[n_1 \ln X_1 + n_2 \ln X_2 \ldots\right] \\ &= -R\sum n_i \ln X_i \\ &= -R\sum X_i \ln X_i \qquad (\because X_i \propto n_i) \qquad (18) \end{aligned}$$

It is interesting to note that mole fraction X_i of any gas in a mixture must be less than unity, its logarithm is negative, hence ΔS_{mixing} as defined by Eq. (18) is always positive. Hence, the mixing of two or more gases is always accompanied by an increase in entropy.

Solved examples

1. Calculate the entropy of mixing of 1 mole of N_2 and 2 moles of O_2, assuming the gases to be ideal. Express the result in S.I. units.

Solution

$$\Delta S_{\text{mix}} \text{ per mole} = -2.303R\left[n_1 \log X_1 + n_2 \log X_2\right]$$

$$X_1 = \frac{\text{moles of } N_2}{\text{Total number of moles}} = \frac{1}{3} \;; X_2 = \frac{\text{moles of } O_2}{\text{Total number of moles}} = \frac{2}{3}$$

$$\Delta S_{mix} = -2.303\times 8.314\left[\frac{1}{3}\log\frac{1}{3}+\frac{2}{3}\log\frac{2}{3}\right] \text{ J K}^{-1}$$

$$= +2.303\times 8.314\left[\frac{1}{3}\log 3+\frac{2}{3}\log\frac{3}{2}\right] \text{ J K}^{-1}$$

$$= 2.303\times 8.314(0.1590+0.1174) \text{ J K}^{-1}$$

$$= 5.29 \text{ J K}^{-1}$$

$$\text{for 3 moles } \Delta S_{mix} = 3\times 5.29 = 15.87 \text{ J K}^{-1}$$

2. At NTP, 2.8 L of oxygen were mixed with 19.6 L of hydrogen. Calculate the increase in entropy, assuming ideal gas behavior.

Solution

Here,

$$n_1 = \frac{2.8 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.125 \text{ mol}; \quad n_2 = \frac{19.6 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.875 \text{ mol}$$

$$X_1 = \frac{0.125}{0.125+0.875} = 0.125 \text{ and } X_2 = \frac{0.875}{0.125+0.875} = 0.875$$

$$\Delta S_{mixing} = -R\times 2.303\left[n_1\log X_1 + n_2\log X_2\right]$$

$$= -8.314 \text{ J K}^{-1}\text{ mol}^{-1}\times 2.303\,[0.125 \text{ mol} \log 0.125 + 0.875 \text{ mol} \log 0.875]$$

$$= -8.314\times 2.303\,[-0.1129 - 0.0507]$$

$$= 8.314\times 2.303\times(-0.1636) = 3.132 \text{ J K}^{-1}$$

3. The mixing of gases is always accompanied by an increase in entropy. Show that in the formation of a binary mixture of two ideal gases the maximum entropy increase results when $X_1 = X_2 = 0.5$

Solution

For a binary mixture the entropy per mole of the mixture formed is given by

$$\Delta S_{mixing} = -R\left[X_1 \ln X_1 + X_2 \ln X_2\right]$$

$$= -R\left[X_1 \ln X_1 + (1-X_1)\ln(1-X_1)\right]$$

For entropy of mixing to be maximum, the first derivative $\dfrac{\delta(\Delta S_{mixing})}{\delta X_1}$ should be zero and the second derivative should be negative. Differentiating ΔS_{mixing} with respect to X_1 we get

$$\frac{\delta(\Delta S_{mixing})}{\delta X_1} = -R\left[\ln X_1 + \frac{X_1}{X_1}+\frac{1-X_1}{1-X_1}(-1)+(-1)\ln(1-X_1)\right]$$

$$-R(\ln X_1 + 1 - 1) - \ln(1-X_1) = 0$$

$$\text{or } \ln X_1 + 1 - 1 - \ln(1-X_1) = 0$$

$$\text{or}\quad \ln\frac{X_1}{1-X_1}=0 \qquad \text{or}\quad X_1=1-X_1$$

$$2X_1=1 \qquad X_1=1/2=0.5$$

And hence X_2 = 1–0.5 = 0.5.

Practice problems

1. 1 mole of H_2 and 9 moles of N_2 are mixed at 298 K and 1 atmosphere. Assuming the ideal behavior of the gas, calculate the entropy of mixing per mole of the mixture formed.
[Ans 2.704 J K^{-1} mol^{-1}]

15.21 Free Energy Function (G) and Work Function(A)

The feasibility of a process or chemical reaction cannot be determined by enthalpy change or entropy change alone. Both the functions are essential to predict the spontaneity or feasibility of a chemical reaction. The functions which incorporate both energy and entropy change are the free energy function and work function represented by G and A respectively . Both these functions are state functions, that is, their value depends only on the initial and final state of the system. They are given by

$$A = E - TS$$
$$G = H - TS$$

Physical significance of work function Consider an isothermal change from initial state denoted by subscript 1 to the final state denoted by the subscript 2.

$$A_1 = E_1 - TS_1 \quad \text{and} \quad A_2 = E_2 - TS_2$$

Change in work function at constant temperature is given by

$$A_2 - A_1 = (E_2 - E_1) - T\,(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \tag{1}$$

$\because\ \Delta S = \frac{q_{rev}}{T}$, where q_{rev} is the heat taken up when the reaction is carried out in a reversible manner. Substituting the value of ΔS in Eq. (1) we get

$$\Delta A = \Delta E - q_{rev} \tag{2}$$

According to the first law of thermodynamics, for a reversible isothermal process

$$\Delta E = q + w \text{ hence}$$

$$w_{rev} = \Delta E - q_{rev}$$

If work is done by the system it is negative so that

$$-w_{rev} = \Delta E - q_{rev} \tag{3}$$

Comparing Eq. (2) and (3) we get,

$$-\Delta A = w_{rev}$$

Thus, at constant temperature decrease in the function A is equal to the reversible work done by the system. As reversible work is the maximum work that can be obtained from a given thermodynamic change in state, in an isothermal process the decrease in work function is a measure of the maximum work obtainable from the change in state. The work function A is also referred to as Helmholtz free energy or the Helmholtz function .

Similarly considering the free energy function G we have

$$G = H - TS$$

If at constant temperature the thermodynamic functions in the initial and final states are represented G_1, H_1, S_1 and G_2, H_2, S_2 respectively then

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S$$

As studied earlier at constant pressure

$$\Delta H = \Delta E + P\Delta V$$
$$\therefore \Delta G = \Delta E + P\Delta V - T\Delta S$$

$$\text{or } \Delta G = \Delta A + P\Delta V \qquad \because \Delta A = \Delta E - T\Delta S$$

Since ΔA is equal to $-w$ hence,

$$\Delta G = -w + P\Delta V \text{ or } -\Delta G = w - P\Delta V$$

Since $P\Delta V$ gives the work expansion of the gas at constant pressure hence the term $-\Delta G$ is a measure of work other than the work due to change in volume at constant temperature and pressure. This work other than the work due to the change in volume is termed as the net work. thus

$$\text{Net work} = w - P\Delta V = -\Delta G$$

The quantity ΔG is termed as the Gibbs free energy or simply free energy and $-\Delta G$ gives the decrease in free energy. Since ΔG measures work other than the work due to change in volume hence the net work is a measure of the electrical or chemical work.

Variation of free energy on pressure and temperature

By definition,

$$G = H - TS$$

Since $H = E + PV$

$$\therefore\ G = E + PV - TS.$$

By partial differentiation we get

$$dG = dE + PdV + VdP - TdS - SdT \tag{1}$$

From the first law of thermodynamics,

$$dq = dE - dw$$

If the work done is only due to expansion then

$$-dw = PdV$$

$$\therefore\quad dq = dE + PdV$$

$$\text{or}\quad dE = dq - PdV \tag{2}$$

It is assumed that the process is reversible and no work other than that of volume change is occurring, hence

$$dq = TdS$$

Substituting the value of dq in Eq. (2), we get

$$dE = TdS - PdV \tag{3}$$

Putting the value of dE in Eq. (1), we get

$$dG = VdP - SdT \tag{4}$$

This equation takes different forms under different conditions

(i) **At constant temperature**, that is, when $dT = 0$, Eq. (4) takes the form

$$dG = VdP$$

$$\text{or}\quad \left(\frac{\partial G}{\partial P}\right)_T = V \tag{5}$$

(ii) **At constant pressure**, that is, when $dP = 0$, Eq. (4) takes the form

$$dG = -SdT$$

$$\text{or}\quad \left(\frac{\partial G}{\partial T}\right)_P = -S \tag{6}$$

Free energy change with pressure for an ideal gas

At constant temperature, it follows that

$$dG = VdP \tag{7}$$

If the pressure changes from P_1 to P_2, the corresponding free energy will change from G_1 to G_2. Integrating Eq. (7) between these limits, we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP \tag{8}$$

for an ideal gas

$$V = \frac{nRT}{P}$$

Substituting the value of V in Eq. (8), we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

or $\Delta G = G_2 - G_1 = nRT\ln\frac{P_2}{P_1}$

or $$\Delta G = 2.303\ nRT\log\frac{P_2}{P_1} = 2.303\ nRT\log\frac{V_1}{V_2} \tag{9}$$

where V_1 and V_2 are the initial and final volumes, respectively. As G is a state function, Eq. (9) gives free energy change whether the reaction is carried out reversibly or irreversibly.

Solved examples

1. Calculate the free energy change when 4 moles of an ideal gas expands from a pressure of 10 to 1 atm at 25 °C.

Solution

$$\Delta G = 2.303\ nRT\log\frac{P_2}{P_1}$$

Here, n = 4 moles; $R = 8.314\ J\ K^{-1}\ mol^{-1}$; T = 273 + 25 = 298 K; $P_1 = 10$ atm; $P_2 = 1$ atm.

$$\Delta G = 2.303 \times 4 \times 8.314 \times 298\ \log\frac{1}{10}$$

$$= -22823.39\ J$$

2. ΔG for a reaction at 300 K is –16 kcal; ΔH for the reaction is –10 kcal. What is the entropy of the reaction? What will be ΔG at 330 K?

   Solution

   (i) $\Delta G = \Delta H - T\Delta S$

   $$\text{or}\quad \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-10\ \text{kcal} + 16\ \text{kcal}}{300\,\text{K}} = 0.02\ \text{kcal}\,\text{K}^{-1} = 20\ \text{cal}\,\text{K}^{-1}$$

   (ii) ΔG at 330 K = $\Delta H - T\Delta S$

   $$= -10\ \text{kcal} - 330\ \text{K} \times 0.02\ \text{kcal K}^{-1} = -16.6\ \text{kcal.}$$

3. Calculate ΔG for the conversion of 1 mole of water at 100 °C and 1 atm to steam at 100 °C and 0.5 atm pressures.

   Solution

   ΔG = (ΔG for the conversion of H_2O (l) at 100 °C and 1 atm to steam at 100 °C and 1 atm).
   + (ΔG for the transition of steam at 100 °C from 1 atm to 0.5 atm).

   The first term on the RHS is zero, as H_2O (l) and H_2O (g) are in equilibrium at 100 °C and 1 atm pressure.

   The second term is $= 2.303\ nRT\ \log\dfrac{P_2}{P_1}$

   $$\Delta G = 2.303 \times 1 \times 1.987 \times 373 \times \log_{10}\frac{0.5}{1}$$

   $$= 2.303 \times 1 \times 1.987 \times 373 \times (-0.3010)$$

   $$= -513.82\ \text{cal}$$

Practice problems

1. 4 mole of an ideal gas is compressed isothermally at 300 K from 2.02×10^5 N m^{-2} to 4.04×10^5 N m^{-2} pressure. Calculate the free energy change for the process. [Ans 6916.63 J]

2. One mole of an ideal gas at 27 °C expands isothermally and reversibly from initial volume of 2 dm^3 to a final volume of 20 dm^3 against a pressure that is gradually reduced. Calculate q, w, ΔE, ΔH, ΔA, ΔG and ΔS.
   [Ans q = 5744 J mol^{-1}; w = –5744 J mol^{-1}; ΔE= 0; ΔH= 0; ΔA = –5744 J mol^{-1}.
   ΔG = –5744 J mol^{-1} and ΔS = 19.15 J K^{-1} mol^{-1}]

3. Calculate ΔG for the formation of H_2O (l) from its elements at 25 °C. ΔH_f = –286 kJ. Entropies of H_2 (g), O_2 (g) and H_2O (g) are 130.6, 205.0 and 70.3 J K^{-1} mol^{-1}, respectively.
   [Ans ΔG = –237.5 kJ]

15.22 Gibbs–Helmholtz Equation

At constant pressure, the change of free energy with temperature is given by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{10}$$

Suppose a system changes reversibly and isothermally from state 1 to state 2. If the free energy and entropy of the system in state 1 are G_1 and S_1 respectively, and in state 2 are G_2 and S_2 respectively, then the entropy change of the system is given by

$$\Delta S = S_2 - S_1 \tag{11}$$

From Eq. (10) we can write

$$S_1 = -\left(\frac{\partial G_1}{\partial T}\right)_P \quad \text{and} \quad S_2 = -\left(\frac{\partial G_2}{\partial T}\right)_P$$

Substituting the values of S_1 and S_2 in Eq. (11) we get

$$\Delta S = -\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$$

$$\text{Or} \quad \begin{aligned} &\text{or} \quad \Delta S = -\left(\frac{\partial (G_2 - G_1}{\partial T}\right)_P \\ &\text{or} \quad \Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \end{aligned} \tag{12}$$

For an isothermal process, $\Delta G = \Delta H - T\Delta S$

Substituting the value of ΔS from Eq. (12) in this equation we get,

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad \text{......(13)} \tag{13}$$

This equation was derived by J.W. Gibbs and H. Von Helmholtz and is known as the **Gibbs–Helmholtz equation**

A corresponding equation for the work function A and internal energy E for an isothermal reversible process at constant volume yields another form of the Gibbs–Helmholtz equation –

$$\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_V \tag{14}$$

Solved problems

1. For the following reaction

$N_2(g) + 3\,H_2(g) \rightarrow 2NH_3\,(g)$

The free energy change at 25 °C and 35 °C are –3.98 and – 3.37 kcal. Calculate the heat of reaction at 35 °C.

Solution

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\text{also}\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{G_2 - G_1}{T_2 - T_1}$$

$$\text{Here}\;\; G_1 = -3.98\text{ kcal};\quad G_2 = -3.37\text{ kcal}$$

$$T_1 = 273 + 25 = 298\,\text{K};\;\; T_2 = 273 + 35 = 308\,\text{K}$$

$$\therefore \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-3.37 - (-3.98)}{308 - 298} = \frac{0.61}{10} = 0.061$$

At 35 °C ΔG = –3.37 kcal;   T = 308 K.

$$-3.37 = \Delta H + 308(0.061)$$

$$\Delta H = -3.37 - 18.79 = -22.16\text{ kcal}$$

2. For the following reaction

H_2 (g) + ½ O_2 (g) → H_2O (l)

The value of enthalpy change and free energy change are –68.32 and –56.69 kcal respectively at 25 °C. Calculate the value of free energy change at 30 °C.

Solution

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\text{Here}\;\; \Delta G = -56.69\text{ kcal};\;\; \Delta H = -68.32\text{ kcal}\quad T = 273 + 25 = 298\,\text{K}$$

$$\therefore \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-56.69 + 68.32}{298} = 0.039$$

Assuming that $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ remains constant over this range of temperature, at 30 °C we can write

$$\Delta G = -68.32 + 303 \times 0.039$$

$$= -68.32 + 11.81$$

$$= -56.51\text{ kcal}$$

Practice problems

1. The free energy change for a reaction is –86.5 kJ per mole at 298 K and –83.50 kJ per mole at 308 K. Calculate the enthalpy change (ΔH) for the reaction at 303 K.

[Ans = –175.9 kJ]

2. Calculate ΔA and ΔG for the reversible compression of one mole of an ideal gas from 2 atm to 100 atm at 30.2 °C. [Ans ΔA = 2357.25 cal; ΔG = 2357.25 cal]

15.23 Claypeyron–Clausius Equation

This equation finds application in one component and in the two-phase systems. Let us consider two phases A and B of the same component in equilibrium with each other at constant temperature T and pressure P. This equilibrium may be represented as

$$A \rightleftharpoons B$$

Suppose free energies per mole of the substance in the two phases A and B are G_A and G_B, respectively. As the system is in equilibrium, there is no change in free energy, that is,

$$G_A = G_B \tag{1}$$

If the temperature is raised to T + dT, the pressure P will increase to P + dP. For this change, the molar free energy becomes $G_A + dG_A$ and $G_B + dG_B$, respectively.

As the two phases are in equilibrium,

$$G_A + dG_A = G_B + dG_B \tag{2}$$

As for this phase change the work done is only because of the volume change, the change in energies dG_A and dG_B may be calculated by the equation

$$dG = V.dP - S.dT \tag{3}$$

Therefore, it can be written as

$$dG_A = V_A dP - S_A dT \tag{4}$$

$$dG_B = V_B dP - S_B dT \tag{5}$$

V_A and V_B are the molar volumes of the phases A and B respectively, and S_A and S_B are their corresponding enthalpies. Hence,

$$V_A dP - S_A dT = V_B dP - S_B dT$$

or
$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A} \tag{6}$$

where Δ S = molar entropy change and $V_B–V_A$ is the change in volume when 1 mole of substance changes from A to B.

From Gibbs–Helmholtz equation

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

∴ $\Delta G = 0$ (Eq. 1). Hence, Eq. (7) may be written as

$$\Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta S = \frac{\Delta H}{T} \quad .....(8) \quad (8)$$

Placing this in Eq. (6) we get

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_B - V_A)}, \quad (9)$$

This is the Claypeyron – Clausius equation. ΔH represents the change in enthalpy for phase change at temperature T and $\frac{dP}{dT}$ represents the rate of change of pressure with temperature.

Integrated form of Claypeyron – Clausius equation for liquid – vapor equilibrium

In liquid vapor equilibrium $V_V >> V_L$, hence $V_V - V_L \approx V_V$
The Claypeyron–Clausius equation takes the form

$$\frac{dP}{dT} = \frac{\Delta H_V}{TV_V} \quad (10)$$

Assuming the vapours behave ideally,

$$PV_V = RT \quad \text{or} \quad V_V = \frac{RT}{P}$$

Inserting this value in Eq. (10)

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_V}{RT^2}$$

Integrating, on the assumption that ΔH_V is constant over a small temperature change, we get

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_V}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where P_1 and P_2 are the vapor pressures at T_1 and T_2 respectively. Molar heat of vaporisation at different temperatures can be computed with this equation.

Solved examples

1. The latent heat of vaporisation of benzene at its boiling point (80 °C) is 7413 cal mol^{-1}. What is the vapor pressure of benzene at 27 °C.

Solution

$\Delta H_V = 7413 \text{ cal mol}^{-1}$; $T_1 = 80\text{ °C} = 353 \text{ K}$; $P_1 = 1 \text{ atm} = 760 \text{ mm Hg}$

$T_2 = 27\text{ °C} = 300\text{ K}$; $P_2 = ?$

$$\log\frac{P_2}{P_1} = \frac{\Delta H_V}{2.303\ R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log\frac{P_2}{760 \text{ mm Hg}} = \frac{7413 \text{ cal mol}^{-1}}{2.303\times 1.987 \text{ cal mol}^{-1}\ K^{-1}}\left[\frac{300-353}{300\times 353}\right]$$

$$= \frac{7413\times(-53)}{2.303\times 1.987\times 300\times 353} = -0.8107$$

$$\log\frac{760 \text{ mm Hg}}{P_2} = 0.8107$$

$$\text{or} \quad \frac{760 \text{ mm Hg}}{P_2} = \text{Antilog } 0.8107 = 6.4670$$

$$\text{Hence} \quad P_2 = 760/6.4670 = 117.52 \text{ mm Hg}$$

2. If the atmospheric pressure is 535 mm of mercury, find the temperature at which water will boil. Latent heat of vaporisation of water is 545.5 cal/g.

Solution

$P_1 = 535 \text{ mm Hg}$; $P_2 = 1 \text{ atm} = 760 \text{ mm Hg}$

$T_1 = ?$; $T_2 = 100 + 273 = 373 \text{ K}$

$\Delta H_v = 545.5 \text{ cal/g} = 545.5 \times 18 \text{ cal/mol} = 9819 \text{ cal mol}^{-1}$

$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

$$\log\frac{P_2}{P_1} = \frac{\Delta H_V}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log\frac{760}{535} = \frac{9819 \text{ cal mol}^{-1}}{2.303\times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}}\left[\frac{1}{T_1} - \frac{1}{373}\right]$$

$$\frac{1}{T_1} - \frac{1}{373} = \frac{0.1524\times 2.303\times 1.987}{9819} = 0.00007102$$

$$\text{or} \quad \frac{1}{T_1} - 0.002681 \text{ K}^{-1} = 0.00007102 \text{ K}^{-1}$$

$$T_1 = \frac{1}{0.00275202} = 363.37 \text{ K}$$

Practice problems

1. The latent heat of vaporisation of water is 540 cal/g at about 100 °C. Calculate the pressure at which water must be heated to produce superheated steam at 150 °C. [Ans 4.709 atm]

15.24 Vant Hoff Isotherm

Consider the general reaction

$$A + B \rightarrow C + D \qquad (1)$$

We know that

$$dG = VdP - SdT$$

At constant temperature $(dG)_T = VdP$

The free energy change for 1 mole of any gas at constant temperature is given by

$dG = VdP$ $\because$ for an ideal gas $PV = RT$ or $V = RT/P$

$$\text{Hence } dG = RT.\frac{dP}{P}$$

Integrating,

$$\int dG = RT\int\frac{dP}{P}$$

$$G = G^{\circ} + RT\ln P \qquad (2)$$

Here, G° is the integration constant and is known as the standard free energy, that is, G° = G when P =1 atm.

Let the free energy per mole of A, B, C, D at their respective pressures P_A, P_B, P_C, P_D are G_A, G_B, G_C, G_D respectively. Then the free energy of A per mole at temperature T is

$$G_A = G_A^{\circ} + RT\ln P_A$$

Similarly, free energies of B, C and D are as follows:

$$G_B = G_B^{\circ} + RT\ln P_B$$
$$G_C = G_C^{\circ} + RT\ln P_C$$
$$G_D = G_D^{\circ} + RT\ln P_D$$

The change in free energy ΔG is

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = [(G_C + G_D) - (G_A + G_B)];\ \text{hence,}$$

$$\Delta G = \left(G_C^{\circ} + RT\ln P_C + G_D^{\circ} + RT\ln P_D\right) - \left(G_A^{\circ} + RT\ln P_A + G_B^{\circ} + RT\ln P_B\right)$$

$$= (G_C^{\circ} + G_D^{\circ} - G_A^{\circ} - G_B^{\circ}) + RT\ln\frac{P_C \times P_D}{P_A \times P_B}$$

$$G = \Delta G^{\circ} + RT\ln\frac{P_C \times P_D}{P_A \times P_B} \qquad (3)$$

ΔG^0 = Standard free energy of reaction (1);

but at equilibrium $\Delta G = 0$.

Therefore, $0 = \Delta G^\circ + RT\ln K_{eq}$

$$\text{or } \Delta G^0 = -RT\ln K_{eq} \quad \ldots\ldots \; 4 \qquad (4)$$

where $K_{eq} = \dfrac{P_C \times P_D}{P_A \times P_B}$

On substituting this value of ΔG° in Eq. (3)

$$\Delta G = -RT\ln K_{eq} + RT\ln\frac{P_C \times P_D}{P_A \times P_B} \qquad (5)$$

For the general reaction; aA + bB → cC + dD; the Eq. (5) becomes

$$\Delta G = -RT\ln K_{eq} + RT\ln\frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \qquad (6)$$

This expression is termed as the Van't Hoff isotherm. It gives a quantitative relationship for the free energy change in a chemical reaction.

Van't Hoff isochore It deals with the variation of equilibrium constant with temperature.

$$\Delta G^0 = -RT\ln K_{eq}$$

$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT} = \frac{-(\Delta H^\circ - T\Delta S^\circ)}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\therefore \ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad \text{and} \quad \ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

$$\text{or} \quad \ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \quad \text{or}$$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad (7)$$

This expression, called the Van't Hoff isochore, can be used to calculate equilibrium constant at T_2 if its value at T_1 is known.

Solved example

1. The equilibrium constant for the reaction

   H_2 (g) + S (s) $\rightleftharpoons$ H_2S (g) is 18.5 at 925 K and 9.25 at 1000 K. Calculate standard enthalpy of the reaction. Also calculate ΔG^0 and ΔS^0 at 925 K.

Solution

From Van't Hoff isochore,

$$\log\frac{K_2}{K_1}=\frac{\Delta H^\circ}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$\log\frac{K_{1000K}}{K_{925K}}=\frac{\Delta H^\circ}{2.303\times 8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1000-925}{925\times 1000}\right)$$

$$\log\frac{9.25}{18.5}=\frac{\Delta H^\circ}{2.303\times 8.314}\left(\frac{75}{925000}\right)$$

$$\Delta H^\circ=-71080\ \text{J mol}^{-1}=-71.08\ \text{kJ mol}^{-1}$$

$$\begin{aligned}\text{now;}\ \ \Delta G^\circ &= -2.303RT\log K_{eq}\\ &= -2.303\times 8.314\ \text{J mol}^{-1}\times 925\ \log 18.5\\ &= -22400\ \text{J mol}^{-1}\\ &= -22.4\ \text{kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \frac{\Delta H^\circ-\Delta G^\circ}{T}\\ &= \frac{(-71080+22400)\ \text{J mol}^{-1}}{925}=-52.6\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Practice problems

1. The equilibrium constant of the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at 528 °C is 98.0 and at 680 °C is 10.5. Find the heat of reaction. [Ans – 93273.33 J]
2. The equilibrium constant K for the reaction

   $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.064×10^{-4} at 400 °C and 0.144×10^{-4} at 500 °C. Calculate the mean heat of formation of 1 g mol of ammonia from its elements in this temperature range.

   [Ans $\Delta H = -12575$ cal]

15.25 Maxwell's Thermodynamic Relations

We know that

$$H = E + PV$$

$$A = E - TS.$$

and G = H–TS or G = E + PV – TS

The differential forms of these equations can be written as

$$dH = dE + PdV + VdP \tag{1}$$

$$dA = dE - TdS - SdT \tag{2}$$

$$dG = dE + PdV + VdP - TdS - SdT \tag{3}$$

As dE= TdS–PdV, substituting the value of dE in Eqs. (1), (2) and (3), we get

$$dH = TdS + VdP \tag{4}$$

$$dA = -SdT - PdV \tag{5}$$

$$dG = VdP - SdT \tag{6}$$

The above three Eqs. (4), (5) and (6) along with the equation dE = TdS – PdV are the four fundamental equations of thermodynamics.

Derivation of Maxwell's equations

If an exact differential dZ can be put in the form $dZ = Mdx + Ndy$ then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ is known as the Euler's relation. This can be used to obtain the Maxwell's relations.

From the fundamental thermodynamic equations, we have

$$dH = TdS + VdP$$

compare with $dZ = Mdx + Ndy$

By the Euler relation,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{7}$$

$$dA = -SdT - PdV$$

using Euler's relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{8}$$

$$dG = VdP - SdT$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{9}$$

$$dE = TdS - PdV$$

on comparing with Euler's relation we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{10}$$

These above four equations are known as Maxwell's relations. The relations (8) and (9) are referred to as isothermal relations and the relations (7) and (10) are isoentropic or adiabatic.

15.26 Spontaneity and Equilibrium

Equilibria and spontaneity change can be explained in terms of various thermodynamic functions. Entropy (S) and free energy (G) are the important thermodynamic functions used for predicting equilibrium.

Entropy as a criterion of equilibrium and spontaneity change

By the first law of thermodynamics dq = dE + PdV, where dq is the quantity of heat absorbed and dE is the change in the internal energy of the system and PdV, the mechanical work done by the system. Suppose the process is reversible

$$dq_{rev} = dE + (PdV)_{rev}$$

$$\text{but,}\quad dS = \frac{dq_{rev}}{T} \qquad \therefore dS = \frac{dE + (PdV)_{rev}}{T} \tag{1}$$

If the process is irreversible, then

$$\frac{dq_{irrev}}{T} = \frac{dE + (PdV)_{irrev}}{T} \tag{2}$$

In both these expressions, dE is the same, as E is a thermodynamic property that depends only on the initial and final states of the system and not on the path, whether reversible or irreversible.

If the reversible process occurs at constant internal energy (E) and volume (V), then from equation, $\partial S_{E,V} = 0$. As the condition for reversible change is also the condition for equilibrium, we have

$$\partial S_{E,V} = 0 \tag{3}$$

Comparing the right hand sides of the Eqs. (1) and (2), $(PdV)_{rev} > (PdV)_{irrev}$, as for the given initial and final states, the work done is maximum for a reversible process.

$$\therefore dS > \frac{dq_{irrev}}{T} \quad \text{or} \quad dS > \frac{dE + (PdV)_{irrev}}{T}$$

$$\text{or} \quad \partial S_{E,V} > 0 \tag{4}$$

This is the condition for a spontaneous process. Equations (3) and (4) are combined and the condition for spontaneous change and equilibrium are expressed as

$$\partial S_{E,V} \geq 0$$

In an analogous manner, it would follow from Eqs. (1) and (2), that for equilibrium $\partial E_{S,V} = 0$ and for a spontaneous process $\partial E_{S,V} < 0$. Combining the two conditions,

$$\partial E_{S,V} \leq 0$$

Thus, in any spontaneous process taking place at constant E and V, the entropy increases ultimately reaching a maximum value at equilibrium. Once the equilibrium is reached, there occurs no more change in entropy. A system with constant E and V is also known as an isolated system and the universe is one such system. As spontaneous processes continuously occur in the universe, the entropy of the universe is increasing.

Similarly, in any spontaneous process taking place at constant S and V, the internal energy goes on decreasing, ultimately attaining a minimum value at equilibrium.

Gibbs free energy (G) as a criterion of equilibrium and spontaneous change

By definition,

$$G = H - TS$$

$$= E + PV - TS$$

where H is the enthalpy of the system

For an infinitesimal change.

$$\begin{aligned} dG &= dE + PdV + VdP - TdS - SdT \\ &= \underbrace{VdP - SdT}_{\text{I term}} + \underbrace{dE + PdV - TdS}_{\text{II term}} \end{aligned}$$

At constant temperature and pressure, the first term becomes zero and hence $\partial G_{T,P} = dE + PdV - TdS$. If we assume the work done by the system to be work of expansion (PdV) then

$$dq = dE + PdV$$

$\therefore \partial G_{T,P} = dq - TdS$. If the process is reversible then $dq = dq_{rev} = TdS$ and hence

$$\partial G_{T,P} = 0$$

As already indicated, the condition for a reversible process is also a condition for equilibrium, hence for equilibrium

$$\partial G_{T,P} = 0$$

$dq_{rev} = dE + (PdV)_{rev}$ and

$dq_{irrev} = dE + (PdV)_{irrev}$

since $(PdV)_{rev} > (PdV)_{irrev}$

Hence $dq_{rev} > dq_{irrev}$

Consider the expression-

$\partial G_{T,P} = dq - TdS$

For irreversible process.

$\partial G_{T,P} = dq_{irrev} - TdS$

But, $dq_{irrev} < dq_{rev}$

and $dq_{rev} = TdS$

$\therefore dq_{irrev} < TdS$

Hence, for an irreversible or spontaneous process and equilibrium $\partial G_{T,P} < 0$

Combining the conditions for spontaneous process and equilibrium,

$$\partial G_{T,P} \leq 0$$

Thus, for any spontaneous process taking place at constant temperature and pressure, the free energy of the system decreases, ultimately attaining a minimum value at equilibrium.

In an analogous manner, the conditions for spontaneous change and equilibrium can be expressed in terms of the Helmholtz free energy (A) as

$$\partial A_{T,V} \leq 0 \qquad \text{where} \qquad A = E - TS$$

Entropy and free energy criteria compared

The free energy criteria for spontaneous change and equilibrium are more useful than the entropy criteria. Recapitulating these criteria,

$$\partial S_{E,V} \geq 0 \qquad \text{and} \qquad \partial G_{T,P} \leq 0$$

It is difficult to keep internal energy of a system constant, whereas the temperature and pressure can be easily kept constant. Hence, G has a greater utility. This point can be viewed in an alternative manner. A system with constant E, V is an isolated system, which may be taken to constitute both the system and the surrounding. Hence, in using the entropy criterion, it is essential to make measurements on both system and surroundings. However, it is rather difficult to make measurement on the surroundings. Hence, the criterion of entropy is less useful.

Solved examples

1. Enthalpy and entropy changes of a reaction are 40.63 kJ mol^{-1} and 108.8 J K^{-1} mol^{-1}, respectively. Predict the feasibility of the reaction at 27 °C.

Solution

$\Delta H = 40.63$ kJ $mol^{-1} = 40630$ J mol^{-1}; $\Delta S = 108.8$ J K^{-1} mol^{-1}; $T = 27+273 = 300$ K

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

$$= 40630 - 300 \times 108.8 = +7990 \text{ J mol}^{-1} = 7.99 \text{ kJ mol}^{-1}$$

As ΔG is positive, the reaction is not feasible.

2. ΔH and ΔS for the reaction,

$Ag_2O\,(s) \rightarrow 2Ag(s) + ½\,O_2\,(g)$

are 30.56 kJ mol^{-1} and 66.0 J K^{-1} mol^{-1}, respectively. Calculate the temperature at which the free energy change for the reaction will be zero. Predict whether the forward reaction will be favored above or below this temperature.

Solution

According to Gibb Helmholtz equation,

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

At equilibrium, $\Delta G = 0$ so that

$$0 = \Delta H - T\Delta S \qquad \text{or} \qquad \Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} \quad \text{Here,} \quad \Delta H = 30.56 \text{ kJ mol}^{-1} = 30560 \text{ J mol}^{-1} \quad \text{and } \Delta S = 66 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = \frac{30560}{66} = 463\,\text{K}$$

In the above reaction, both ΔH and ΔS are positive, therefore the reaction will be spontaneous above 463 K, so that the term $T\Delta S$ becomes greater than ΔH and ΔG becomes negative.

Practice problems

1. For the melting of ice at 25 °C, $H_2O\ (s) \rightarrow H_2O\ (l)$

   The enthalpy of fusion is 6.97 kJ mol^{-1} and entropy of fusion is 25.4 J mol^{-1} K^{-1}. Calculate the free energy change and predict whether the melting of ice is spontaneous or not at this temperature.

   [Ans $\Delta G = -0.6$ kJ mol^{-1}. As ΔG is negative, hence the reaction is spontaneous]

2. The values of ΔH and ΔS for two reactions are given below

   Reaction A $\quad \Delta H = -10.5 \times 10^3$ J mol^{-1}

   $\Delta S = +31$ J K^{-1} mol^{-1}

   Reaction B $\quad \Delta H = -11.7 \times 10^3$ J mol^{-1}

   $\Delta S = -105$ J K^{-1} mol^{-1}

   Predict whether these reactions are spontaneous or not at 298 K.

   [Ans Reaction A: spontaneous; reaction B: non-spontaneous]

Summary

Important thermodynamic relations

1. $\Delta E = q + w$

   Heat (q) absorbed by the system = + q

   Heat released to the surrounding = – q

   Work done by the system (work expansion) = –w

   Work done on the system (work compression) = +w.

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

   $q_P = q_V + P\Delta V$

3. $C_P = \left(\frac{\partial H}{\partial T}\right)_P$, $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

For an ideal gas

- $\left(\frac{\partial E}{\partial P}\right)_T = 0$, $\left(\frac{\partial E}{\partial V}\right)_T = 0$, $\left(\frac{\partial H}{\partial P}\right)_T = 0$ $\left(\frac{\partial H}{\partial V}\right)_T = 0$
- $PV = nRT$
- $C_P - C_V = R$

Isothermal process for an ideal gas

- $\Delta E = 0; \Delta H = 0, q = w$
- $w_{rev} = -nRT\ln\frac{V_2}{V_1} = -nRT\ln\frac{P_1}{P_2} = -2.303nRT\log_{10}\frac{V_2}{V_1}$
- $w_{irrev} = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1) = nRT\left(1 - \frac{P_1}{P_2}\right)$
- Work done in isochoric process = 0 $\because dV = 0$
- Work done against zero external pressure = 0 (if a gas expands against vacuum no work is done).

Adiabatic processes for an ideal gas

- $w = \Delta E$ $\because q = 0$
- **For reversible process,**
- $PV^{\gamma} = \text{constant}$; $TV^{\gamma-1} = \text{constant}$; $T^{\gamma} / P^{\gamma-1} = \text{constant}$
- **Work done in a reversible process**
- $w = nC_vT_1\left(\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} - 1\right)$
- $w = nC_vT_1\left(\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right)$
- $w = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$
- $R = C_P - C_V$

- $\gamma = \frac{C_P}{C_V}$
- γ for a monoatomic gas = 5/3.
- For monoatomic gas $C_P = 5 \text{ cal } K^{-1}\text{mol}^{-1}$; $C_V = 3 \text{ cal } K^{-1}\text{mol}^{-1}$
- $-w_{irrev} = nRT_1\left(\frac{T_2}{T_1} - \frac{P_2}{P_1}\right)$
- $\Delta E = P_2\left(\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2}\right)$
- $\Delta H = C_P\left(T_2 - T_1\right) = nRT_1\left(\frac{P_2 - P_1}{P_1}\right)$
- Work (isothermal) > Work (adiabatic)
- **Kirchhoff's equation** = $\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P$
- $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT = \Delta C_P(T_2 - T_1)$
- Joule–Thomson co-efficient $\mu_{J.T} = \left(\frac{\partial T}{\partial P}\right)_H$
- **Second law of thermodynamics**

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat drawn from the source}} = \frac{q_1 - q_2}{q_1}$$

$$= \frac{RT_1 \ln\frac{V_2}{V_1} - RT_2 \ln\frac{V_4}{V_3}}{RT_1 \ln\frac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1} = \frac{q_1 - q_2}{q_1} = \frac{w}{q_1}$$

Entropy

- $\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$
- $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$; $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$
- $\Delta S_{tran} = \frac{q_{rev}}{T}$

Entropy changes for an ideal gas

- $\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$
- $\Delta S = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$
- For isothermal process $\Delta S_T = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2}$
- For isobaric process $\Delta S_P = nC_P \ln\frac{T_2}{T_1}$
- For isochoric process $\Delta S_V = nC_V \ln\frac{T_2}{T_1}$
- Entropy change in heating a solid or liquid $\Delta S = ms\ln\frac{T_2}{T_1}$
- Entropy of mixing. $S_{mix} = -R\sum n_i \ln X_i$

Free energy

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

For ideal gas

- $dG = VdP - SdT$
- $\Delta G = nRT\ln\frac{P_2}{P_1} = nRT\ln\frac{V_1}{V_2}$

Gibb's Helmholtz equation

- $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

  Another form

- $\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_V$

Fundamental thermodynamic equations

- $dE = TdS - PdV$
- $dH = TdS + VdP$
- $dA = -SdT - PdV$
- $dG = -SdT + VdP$

Maxwell's relations

Adiabatic or isentropic

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

For isothermal

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Spontaneity and equilibrium

For spontaneity and equilibrium

$$\partial S_{E,V} \geq 0$$

$$\partial E_{S,V} \leq 0$$

$$\partial G_{T,P} \leq 0$$

$$\partial A_{T,V} \leq 0$$

Claypeyron–Clausius equation

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_B - V_A)}$$

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_V}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Vant Hoff isotherm

$$\Delta G = -RT\ln K_{eq} + RT\ln\frac{P_C \times P_D}{P_A \times P_B}$$

Vant Hoff isochore

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Review Questions

1. Distinguish between
   (i) Open system and closed system
   (ii) Isothermal process and adiabatic process
   (iii) Extensive properties and intensive properties
   (iv) Reversible process and irreversible process
   (v) Homogeneous system and heterogeneous system
   (vi) Isobaric and isochoric processes.
2. State and explain the first law of thermodynamics
3. What do you understand by the term 'Internal energy' and 'Enthalpy' of a system. Show that the heat absorbed by a system at constant volume is equal to the increase in its internal energy, while that absorbed at constant pressure is equal to the increase in enthalpy.
4. What is meant by thermodynamically reversible and irreversible processes? Show that the work done by a system is maximum when it is expanded isothermally and reversibly.
5. Define work. Prove that the work done is path-dependent.
6. Define heat capacity of a system. Show from thermodynamical considerations that for an ideal gas
   (i) $C_v = dE/dT$
   (ii) $C_p = dH/dT$
7. Obtain different relationships between C_p and C_v for any system and then prove that $C_p - C_v = R$ for one mole of an ideal gas.
8. For an ideal gas, prove that

   (i) $\left(\frac{\partial E}{\partial P}\right)_T = 0$

   (ii) $\left(\frac{\partial E}{\partial V}\right)_T = 0$

   (iii) $\left(\frac{\partial H}{\partial P}\right)_T = 0$
9. In an adiabatic reversible expansion of an ideal gas show that
   (i) $PV^{\gamma} = \text{constant}$
   (ii) $PV^{\frac{R}{C_V}} = \text{constant}$
   (iii) $T^{\gamma} / P^{\gamma-1} = \text{constant}$

10. Show that the work of an adiabatic reversible expansion of an ideal gas is less than that of an isothermal reversible expansion.
11. Define the following terms
    (i) Heat of reaction
    (ii) Heat of formation
    (iii) Heat of combustion
    (iv) Heat of neutralisation
    (v) Heat of solution
    (vi) Heat of fusion
    (vii) Heat of vaporisation
    (viii) Heat of sublimation
12. State and explain the following laws of thermochemistry
    (i) Lavoisier and Laplace's laws
    (ii) Hess's law of constant heat summation.
13. Derive the Kirchhoff equation. Explain how it can be utilized to find out the heat of reaction at one temperature if the heat of reaction at another temperature is known.
14. What is enthalpy of a system? How is it related to internal energy? What is the relationship between ΔH and ΔE?
15. Show that Joule–Thomson porous plug experiment is isenthalpic. Obtain an expression for Joule–Thomson coefficient and comment on its sign.
16. What are Joule–Thomson coefficient and inversion temperature? How would an ideal gas behave in a Joule–Thomson experiment?
17. Explain the following
    (i) Entropy and its physical significance
    (ii) Free energy and its physical significance
    (iii) Spontaneous and non-spontaneous processes
18. Give the various statements of the second law of thermodynamics and show that all of them lead to the same goal.
19. Derive the concept of entropy from the second law of thermodynamics.
20. Derive the expression for the efficiency of the heat engine with the help of Carnot's cycle. Prove that the efficiency of a heat engine is always less than unity.
21. Derive the following expression for the change in entropy of an ideal gas

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R \ln\frac{V_2}{V_1}$$

22. Prove thermodynamically that in an isothermal spontaneous expansion process the entropy is always increasing.
23. Derive an expression for the entropy change during mixing of ideal gases.

24. Derive the Gibbs–Helmholtz equation
25. Prove that

$$\ln\frac{P_2}{P_1}=\frac{\Delta H_V}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

26. What is meant by Van't Hoff reaction? Derive an expression for the reaction isotherm of the general reaction.

$aA + bB \rightarrow cC + dD$

27. Explain the concept of Helmholtz free energy and Gibb's free energy. Describe the relationship between the two.
28. If dE= TdS–PdV, prove that

$$\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial P}{\partial S}\right)_V$$

29. What is spontaneity of a reaction? Describe the criteria for a chemical reaction to be spontaneous.
30. Derive the various forms of Maxwell's relations.

Multiple Choice Questions

1. A wall which allows neither matter nor energy to pass through it is called
   (a) A rigid wall (b) An impermeable wall
   (c) Adiabatic wall (d) Diathermal wall
2. Which of the following is not an intensive property
   (a) Volume (b) Pressure
   (c) Temperature (d) Viscosity
3. Which of the following is not a extensive property
   (a) Heat capacity (b) Enthalpy
   (c) Entropy (d) Chemical potential
4. A thermodynamic process occurring at constant temperature is
   (a) Isobaric process (b) Isochoric process
   (c) Isothermal process (d) Adiabatic process
5. When a gas is subjected to adiabatic expansion, it gets cooled due to
   (a) Loss of kinetic energy (b) Fall in temperature
   (c) Decrease in velocity (d) Energy is used in doing work

6. Which of the following expresses the first law of thermodynamics

(a) $w = q + \Delta E$ (b) $\Delta E = q + w$

(c) $q = E_2 - E_1 + w$ (d) All of the above

7. For a reversible process the value of ΔS is given by the expression

(a) q_{rev} / T (b) $T + q_{rev}$

(c) $\Delta H / \Delta T$ (d) $q_{rev} \times T$

8. Heat and temperature are

(a) Intensive properties

(b) Extensive properties

(c) Extensive and intensive properties respectively

(d) None of the above

9. According to the second law of thermodynamics heat is partly converted into useful work and part of it

(a) Changes into kinetic energy

(b) Changes into electric energy

(c) Is always wasted

(d) None of the above

10. Which of the following expressions is not correct

(a) $\gamma = \frac{C_p}{C_v}$ (b) $TV^{\gamma-1} = \text{constant}$

(c) $\frac{P}{V^{\gamma}} = \text{constant}$ (d) $\frac{T^{\gamma}}{P^{\gamma-1}} = \text{constant}$

11. For a gaseous reaction, $N_2O_4 \rightarrow 2NO_2$

(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$

(c) $\Delta H = \Delta E$ (d) $\Delta H = 0$

12. For the reaction $NaOH + HCl \rightarrow NaCl + H_2O$; the change in enthalpy is called

(a) Heat of reaction (b) Heat of formation

(c) Heat of neutralisation (d) Heat of combustion

13. The enthalpies of combustion of C and CO are –390 kJ mol^{-1} and –278 kJ mol^{-1} respectively. The enthalpy of formation of CO is

(a) 668 kJ mol^{-1} (b) 112 kJ mol^{-1}

(c) –112 kJ mol^{-1} (d) –668 kJ mol^{-1}

14. The enthalpies of formation of N_2O and NO are 82 and 90 kJ mol^{-1}. The enthalpy of reaction $2N_2O\ (g) + O_2\ (g) \rightarrow 4NO(g)$ is

(a) 8 kJ (b) –16 kJ

(c) 88 kJ (d) 196 kJ

15. Calculate the temperature at which ΔG = 5.2 kJ mol^{-1}, ΔH =145.6 kJ mol^{-1} and ΔS =116 kJ mol^{-1} =116 for a chemical reaction
    (a) 130 K
    (b) 1210 K
    (c) 1300 °C
    (d) 130 °C
16. Which of the following process has a negative value of ΔS
    (a) Decomposition of lime
    (b) Dissociation of sugar in water
    (c) Evaporation of water
    (d) Stretching of rubber band
17. One liter–atmosphere is nearly equal to
    (a) 185.0 J
    (b) 101.3 J
    (c) 8.31 J
    (d) 4.18 J
18. A temperature at which gas becomes cooler on expansion is called
    (a) Inversion temperature
    (b) Critical temperature
    (c) Boyle temperature
    (d) Transition temperature
19. Which of the following is not a state function
    (a) Internal energy
    (b) Entropy
    (c) Work
    (d) Heat absorbed under isochoric conditions
20. The free energy $\Delta G = 0$ when
    (a) The system is at equilibrium
    (b) Catalyst is added
    (c) Reactants are initially mixed thoroughly
    (d) Reactants are completely consumed
21. An endothermic reaction A → B proceeds spontaneously. The correct statement is
    (a) ΔH is positive and $T\Delta S > \Delta H$
    (b) ΔH is positive and $\Delta H > T\Delta S$
    (c) ΔS is negative and $T\Delta S > \Delta H$
    (d) ΔG and ΔH both are negative
22. Consider the reactions
    (i) $H_2 + ½ O_2 \rightarrow H_2O$ $\Delta H = -68.39$ kcal
    (ii) $K + H_2O + aq \rightarrow KOH(aq) + ½ H_2$ $\Delta H = -48$ kcal
    (iii) $KOH + aq \rightarrow KOH\ (aq)$ $\Delta H = -14$ kcal
    The heat of formation of KOH is
    (a) $-68.39 + 48 - 14$
    (b) $-68.39 - 48 + 14$
    (c) $68.39 - 48 + 14$
    (d) $68.39 + 48 + 14$
23. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are –3920, –3800 and –24 kJ mol^{-1}. Heat of hydrogenation of cyclohexene is
    (a) –121 kJ mol^{-1}
    (b) –242 kJ mol^{-1}
    (c) +121 kJ mol^{-1}
    (d) +242 kJ mol^{-1}
24. According to the Hess's law
    (a) Energy can be converted from one form to another
    (b) $K_p = K_c RT^{\Delta n}$

(c) The enthalpy change of a given chemical reaction is same whether the process occurs in one or more steps

(d) Energy can be absorbed or released in a reaction but the total energy change of the reacting system and its surroundings remain constant

25. A hypothetical reaction $A \rightarrow 2B$ proceeds via the following sequence of steps

(i) $A \rightarrow C$: $\Delta H = q_1$
(ii) $C \rightarrow D$: $\Delta H = q_2$
(iii) $\frac{1}{2} D \rightarrow B$: $\Delta H = q_3$

The heat of reaction is

(a) $q_1 - q_2 + q_3$ (b) $q_1 + q_2 - 2q_3$
(c) $q_1 + q_2 + 2q_3$ (d) $q_1 + 2q_2 - 2q_3$

26. Which of the following equation represents the fundamental thermodynamic relation

(a) $dH = TdS + VdP$ (b) $dA = - SdT - PdV$
(c) $dG = VdP - SdT$ (d) All the above

27. For Claypeyron–Clausius equation $\log \frac{P_2}{P_1} = \ldots\ldots\ldots$

(a) $\frac{\Delta H_{vap}}{R}$ (b) $\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(c) $\frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ (d) $\frac{-\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

28. $\left[\frac{\partial\left(\frac{\Delta A}{T}\right)}{\partial T}\right]_V = ?$

(a) $-\frac{\Delta E}{T^2}$ (b) $-\frac{\Delta H}{T^2}$

(c) $\frac{\Delta E}{T^2}$ (d) $\frac{\Delta H}{T^2}$

29. Choose the correct expression

(a) $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$ (b) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ (d) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

30. The Joule–Thomson coefficient μ_{JT} is defined by

(a) $\left(\frac{\partial T}{\partial P}\right)_S$ (b) $\left(\frac{\partial P}{\partial T}\right)_S$

(c) $\left(\frac{\partial T}{\partial P}\right)_H$ (d) $\left(\frac{\partial P}{\partial T}\right)_H$

Solution

1	(c)	2	(a)	3	(d)	4	(c)	5	(d)	6	(b)	7	(a)	8	(c)
9	(c)	10	(c)	11	(a)	12	(c)	13	(c)	14	(d)	15	(b)	16	(d)
17	(b)	18	(a)	19	(c)	20	(a)	21	(a)	22	(b)	23	(a)	24	(c)
25	(c)	26	(d)	27	(c)	28	(a)	29	(b)	30	(c)				