Module 5 : Electrochemistry

Lecture 21 : Review Of Thermodynamics

Objectives

In this Lecture you will learn the following

- The need for studying thermodynamics to understand chemical and biological processes.

- Difference between state functions and functions dependent on path.

- The three laws of thermodynamics.

- Applications of the laws of thermodynamics.

- Thermodynamic functions: enthalpy and free energy

- Criteria for spontaneity and equilibrium.

- Maximum work obtainable from systems and free energies.

- Free energy changes and equilibrium constants.

21.1   The scope of Thermodynamics.

Almost all chemical and biological processes involve an interchange of heat and other forms of energy such as pressure-volume work, photons and particles between different parts of the system (a region under consideration with a boundary) as well as with the surroundings. These processes critically depend on temperature.

For example, the activities associated with "life" are nearly restricted to the temperature range of 0° C to 100° C. A quantitative knowledge of these exchanges of heat and work at various temperatures allows us to construct various thermodynamic functions such as energy, entropy and free energy.

These functions in turn allow us to estimate how much useful work can be obtained in a chemical or biochemical process or what will be the concentration of all the species in a mixture (reactants, products and the solvents) when a new equilibrium is established. Thermodynamics plays an important role in our metabolism and as well as during drug action in our body.

21.2   State Functions.

We all know that climbing a mountain top via a very steep path is more strenuous than reaching the same mountain top by a long winding path. This is an illustration of a general feature that work depends on the path followed in a process. The same is true for the heat exchanged between the system and the surroundings. Consider a gas enclosed in a cylinder as shown in Fig 21.1

Fig 21.1 Gas enclosed in a cylinder. Initial volume V_1, and pressure P_1.

The initial volume is V_1 and the pressure is P_1. When the gas is allowed to expand infinitesimally slowly from P_1 to P_2, the gas may be considered to be at equilibrium throughout and the work done is given by

$$w_r = F.dx = (F/A) (Adx) = PdV \qquad (21.1)$$

Here, F is the force on the piston, dx is the increment in the distance moved by the piston and A is the area of the piston. This is the work done by the gas on the surroundings and is positive during an expansion. The work done on the gas, or the work added to the gas is

$$w_g = -PdV \qquad (21.2)$$

The process can be shown graphically as in Fig 21.2 and the area under the curve is the work done by the gas.

Fig 21.2 Reversible and irreversible expansions of an ideal gas. The smooth curve corresponds to a reversible process and the dashed lines represent an irreversible process.

This slow reversible expansion takes an infinitely long time to occur. A three step sequence is shown in Fig 21.2 . The area under the dotted lines is the work done by the gas in the irreversible expansion of the gas.

$$w_{irr} = P_C (V_C - V_1) + P_D (V_D - V_C) + P_E (V_2 - V_D) \qquad (21.3)$$

Ex 21.1

Calculate the work done in the reversible and irreversible expansion of Fig 21.2, if $p_1 = 4$ atm, $p_C = 3$ atm, $P_D = 2$ atm, $P_E = 1$ atm, $V_1 = 10$ lit, $V_C = 13.33$ lit, $V_D = 20$ lit and $V_2 = 40$ lit. Take $T = 298$ K and assume ideal gas behaviour.

The number of moles of gas n = 1.635, 1atm = 1.01325 bar, 1 bar = 10^5 N/m^2, R = 8.314 J/(mol K) = 0.08025 lit atm/ (mol K)

Solution

For an ideal gas, $PV = nRT$

Work done on the surroundings = Pdv

If the system is in equilibrium throughout (reversible process)

P = nRT / V

And w_{sur} = nRT/ V dv = nRT ln V_2 / V_1 = 55.45 lit atm

= 5.62 kJ (Because 1 lit atm = 101.325 J or 1 lit atm = 1.01325 kJ)

In the irreversible process, using eq (21.3),

w_{irr} = 3(13.33-10) + 2(20-13.33) + 1(40-20)

= 43.33 lit.atm

= 4.39 kJ (Because 1 lit atm = 101.325 J or 1 lit atm = 1.01325 kJ)

as

It is seen that the work done in an irreversible process is less than that in a reversible process. Note that the work done on the system = - w_{sur} . In an expansion process, work done on the system is negative.

21.3   The First Law of Thermodynamics

If the process of expansion shown in Fig 21.1 is carried out isothermally (constant temperature T) the gas absorbs a certain amount of heat q. If the process is done reversibly, the work done by the system is maximum (w_{max}) and the heat absorbed by the system is also maximum(q_{max}). If irreversible work is done, then the work done is less than w_{max} and the heat absorbed is also found to be less than q_{max} . These observations lead us to the well known law of conservation of energy in the familiar form of the first law of thermodynamics.

$$\Delta U = q + w \tag{21.4}$$

According to the above law, when a system changes from state 1 (V_1 ,T_1 and P_1) to state 2 (V_2 T_2 and P_2) the change in internal energy, ΔU, is independent of the path. In a cyclic process, wherein the system returns to its original state after passing through several steps, energy is conserved, i.e. it is neither created or destroyed and

$$\Delta U_{cyclic} = 0 \tag{21.5}$$

The energy changes in a system can be determined by knowing the work and the heat.

21.4   Heat Capacities

The capacity to absorb heat in an infinitesimal increment in temperature, $\partial q/ \partial T$ is referred to as the heat capacity. At constant volume, w = -pdV = 0, U = q and the heat capacity is

$$C_V = (\partial U/ \partial T)_V \tag{21.6}$$

In a constant volume process, ΔU = q = q_V and the change in U for a given change in temperature is given by

$$\Delta U = C_V dT \tag{21.7}$$

Analogous to the state function U, other useful state functions can be defined. One such function is enthalpy, H and a change in H is ΔH. Note also that P and V are naturally state functions.

$$H = U + PV \tag{21.8}$$

$$\Delta H = \Delta U + \Delta (PV) \tag{21.9}$$

For a constant pressure process, eq (21.9) becomes

ΔH = q - PdV + d (PV)

= q - PdV + VdP + PdV

= q + VdP

= q, as dP = 0   (21.10)

i.e., the heat absorbed by the system at constant pressure is equal to the enthalpy change in the process. Similar to C_V, we can define a heat capacity at constant pressure C_p by

$$C_p = (\partial H/\partial T)_p$$ (21.11)

A change in enthalpy resulting from a change in temperature at constant pressure is given by

$$\triangle H = C_p \, dT$$ (21.12)

Measurement of heat capacities of substances constituted a major part of the early development of thermodynamics. It enabled the estimation of $\triangle H$ and $\triangle U$ for physical and chemical changes.

For an ideal gas, the equation of state (a relation between P,V and T for a given substance) is PV = nRT where n = number of moles of the gas, R = gas constant and T the absolute temperature. For a monatomic ideal gas, $C_V = 3/2\ R$ and $C_p = 5/2\ R$. In general, heat capacities do have strong temperature dependence and mild pressure dependence

21.5   Entropy

Another state function of fundamental importance is entropy. While both heat and work are forms of energy, it was found that all of heat could not be converted into useful work. Some heat always gets degraded as heat absorbed and lost through the walls of pistons or lost in its flow from hot regions to cold regions without producing anything useful.

Carnot, in the 18 th century showed that even in a fully reversible cyclic process consisting of isothermal and adiabatic (a process wherein q = 0) expansions and compressions, heat cannot be fully converted into work and that the ratio work done by the system (not on the system) to the heat absorbed by the system is always less than 1. All these observations can be summarized through the Clausius inequality.

$$dS \geq dq/T \text{ and } dS = dq_{rev}/T$$ (21.13)

This defines a new state function S, which is the ratio of the reversible heat divided by temperature. Combining eq (21.13) with the first law in a differential form
dU = dq + dw

= TdS - PdV   (21.14)

The subscript rev is not used in 21.14 because whether the process is reversible or not, the difference TdS-PdV is always equal to dU.

21.6   Exact differentials

For a function dependent on two variables x and y, a change in f is brought about by changes in x and y. For an infinitesimal change df we have

$$df = (\partial f/\partial x)_y \, dx + (\partial f/\partial y)_x \, dy$$ (21.15)

The quantity df is called an exact differential if the second partial derivative, taken in two different orders are identical i.e., if eq.(21.17) is satisfied. Here $(\partial f/\partial x)_y$ is the partial derivatives of f with respect to x when y is held constant. Let
df = Mdx + Ndy   (21.16)

where $M = (\partial f/\partial x)_y$ and $N = (\partial f/\partial y)_x$. Now, f is an exact differential if and only if

$$(\partial M/\partial y)_x = (\partial N/\partial x)_y$$ (21.17)

These relations can be easily verified for typical functions such as $f(x, y) = x^3 e^y$. The thermodynamic functions U, H and S are exact differentials, and so are P and V.

Applying eq.(21.17) to dU = TdS-PdV, we have

$$\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V \qquad (21.18)$$

Similarly H = U + PV; dH = TdS − PdV +VdP+ PdV and

$$dH = TdS + VdP \qquad (21.19)$$

and applying eq. (21.17) to eq.(2.19), we have

$$\left(\partial T/\partial P\right)_S = \left(\partial V/\partial S\right)_P \qquad (21.20)$$

Ex 21.2
Show that for one mole of an ideal gas, $C_p - C_V = R$. Use the fact that PV = nRT for an ideal gas and that the energy U of an ideal gas depends only on temperature T and not on volume/pressure.

Solution
Expand U as a function of T and V

$$dU = \left(\partial U/\partial T\right)_V dT + \left(\partial U/\partial V\right)_T dV$$

Take the derivative of this with respect to T at constant p. Note that $(dT/dT)_p = 1$.

$$\left(\partial U/\partial T\right)_p = \left(\partial U/\partial T\right)_V + \left(\partial U/\partial V\right)_T \left(\partial V/\partial T\right)_p = C_V + \left(\partial U/\partial V\right)_T \left(\partial V/\partial T\right)_p$$

Now $C_p = \left(\partial H/\partial T\right)_p$

$$\left(\partial H/\partial T\right)_P = \left(\partial U/\partial T\right)_p + \left(\partial (pV)/\partial T\right)_p = \left(\partial U/\partial T\right)_p + P\left(\partial V/\partial T\right)_p$$

Substitute for $\left(\partial U/\partial T\right)_p$ from the earlier equation

$$C_p = C_V + \left(\partial V/\partial T\right)_p \left(\left(\partial U/\partial V\right)_T + P\right)$$

But , $\left(\partial V/\partial T\right)_p = \partial/\partial T\,(nRT/p) = nR/P$ and $\left(\partial U/\partial V\right)_T = 0$ for an ideal gas

$$C_p = C_V + nR$$

$$= C_V + R \text{ for 1 mole of an ideal gas}$$

21.7 Free Energies
Now we define two more functions called the Helmholtz free energy A and the Gibbs free energy G through the equations.

$$A = U - TS \qquad (21.21)$$
and
$$G = H - TS \qquad (21.22)$$
Substituting for dU and dH, we obtain

$$dA = -SdT - PdV \text{ and} \qquad (21.23)$$

$$dG = -SdT + VdP \qquad (21.24)$$
and applying eq. (21.17), we get

$(\partial S/\partial V)_T = (\partial P/\partial T)_V$ and $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ (21.25)

A great advantage of eq. (21.25) is that the volume and pressure dependence of entropy can be obtained in terms of $\partial P/\partial T$ and $\partial V/\partial T$ which can be very easily measured. Equation (21.18), (21.20) and (21.25) are referred to as Maxwell's relations.

21.8 Standard States

In the case of thermodynamic functions such as energy, enthalpy and free energies, only the difference of these functions between two states of the system can be measured. It is not possible to ascertain the absolute values of these functions. In order to get around this problem, standard states for each substance are defined and the values of these functions in other states are measured with respect to these standard states. The standard state values are represented as U^O , H^O , A^O and G^O.

For solids and liquids, the standard state at each temperature is the state at a pressure of 1 bar. For gases, the standard state at each temperature is the (hypothetical) ideal gas state at a pressure of 1 bar. The changes in thermodynamic functions between the standard states and other states can be calculated using the equations (21.14), (21.19), (21.23) and (21.24). These four equations are equivalent to one another and are referred to as the fundamental equations of thermodynamics. They contain the combined statements of the first and the second laws of thermodynamics.

21.9 The Third Law of Thermodynamics

In the previous section you might have wondered why entropy was not one of the functions in connection with standard states. The reason is not hard to guess .The absolute values of entropy can be ascertained. This follows from the third law of thermodynamics. Entropy is related to disorder or randomness. As the temperature of any system increases, the system changes from solid to liquid and then to gas.

In the gaseous state, the molecules move randomly with respect to each other and there is a great deal of disorder. As the temperature is reduced to very low values, the system generally cools and gets arranged in a definite order. In the case of perfect crystals, there is indeed perfect order and the entropy of such a state is zero.

This is the content of the third law of thermodynamics, which was formulated by Nernst, Planck and others. G.N.Lewis and M Randall stated the third law of thermodynamics as follows. "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, then every substance has a finite positive entropy; but at the absolute zero of temperature, the entropy may become zero and does so in the case of perfectly crystalline substances".

The value of zero for entropy refers to perfect order. Many substances do not condense into perfect crystals even at the absolute zero of temperature. For example, CO at 0 K does not have perfect order. Each CO molecule can be placed as CO or as OC, because both arrangements are energetically equally favorable. The value of entropy can be obtained by the Boltzmann formula, $S = k_B \ln W$, where W is the number of possible arrangements of the molecules. Since each molecule can be arranged in two ways, N_A molecules can be arranged in 2^{N_A} ways. Here N_A is the Avogadro number. Thus the molar entropy of CO at 0K is $N_A k_B$. ln 2 or R ln 2, which is about 1.4 cals/deg/mole. This has been verified experimentally.

Ex 21.3

(a) At low temperatures, the heat capacity of solid KCl may be expressed as $0.006\ T^3$ cal /(deg mol). Calculate the entropy of KCl at 15K, using the third law.

(b) At 234.3 K, the enthalpy of fusion of mercury is 548.6 cal/mol. Calculate the entropy change for the fusion process.

Solution

(a) S_o for KCl may be taken to be 0 at 0 K.

$ds = dq_{rev} = C_p\ dT$ at constant pressure $\backslash \Delta S = {}_0{}^T C_P / T\ dT$

$\Delta S = S_{15} - S_0 = {}_0{}^{15} C_P / T\ dT = {}_0{}^{15} 0.006\ T^3 /T\ dT$

$$= 6.75 \text{ cal/(deg.mol)}$$

(b)   Hg(s) = Hg (l)

$$\triangle S = S_l - S_s = q_{rev} / T = \triangle H/ T = 548.6/234.3 = 2.34 \text{ cal /(deg mol)}$$

21.10   Criteria for spontaneity and equilibrium

One of the great applications of thermodynamics is its role in predicting the direction in which a process will go. Thermodynamics is not able to give any idea about how long it will take for the process to be completed. But knowing the directionality helps in setting up proper temperature and pressure conditions for reactants as well as assembling appropriate electrodes in batteries. From equations (21.12) and (21.14), since TdS $\geq$ dq

$$dS - dq/T \geq 0 \qquad\qquad\qquad (21.26)$$

Here dS and dq refer to the system only and not to the surroundings. When no PV work is done PdV = 0,

$$dU = (dq)_V \text{ and}$$

$$dS - dU/T \geq 0 \text{ or}$$

$$(dS)_{U,V} \geq 0 \text{ or} \qquad\qquad\qquad (21.27)$$

$$(dU)_{S,V} \leq 0 \qquad\qquad\qquad (21.28)$$

Thus, for all natural processes which are irreversible, eq. (21.28) is valid. This is a criterion for a spontaneous or an irreversible process .The criteria are in terms of constant energy or constant entropy, which are difficult to realize in practice. Constant volume/pressure and temperature processes are readily accessible and we look for such suitable criteria now.

At constant pressure $(dq)_P = dH$ and eq.(21.26) becomes

$$dS - (dH)/T \geq 0$$

$$\text{Or } (dS)_{H,P} \geq 0 \text{ or } (dH)_{S,P} \leq 0 \qquad\qquad\qquad (21.29)$$

The Helmholtz free energy is given by eq.(21.21)

$$dA = dU - d (TS)$$

$$= dU - TdS \text{ (at constant temperature)} \qquad\qquad\qquad (21.30a)$$

$$dG = dH - TdS \text{ (at constant temperature)} \qquad\qquad\qquad (21.30b)$$

Since $(dU)_V \leq TdS$ and $(dH)_P \leq TdS$, eq.(21.30a) and eq.(21.30b) become respectively

$$(dA)_{T,V} \leq 0 \qquad\qquad\qquad (21.31)$$

$$(dG)_{T,P} \leq 0 \qquad\qquad\qquad (21.32)$$

The above two equations have extensive applications in chemistry. Note that the equalities apply to equilibria and inequalities in eqns (21.27), (21.28), (21.29), (21.31) and (21.32) apply for spontaneous or irreversible processes

21.11 Maximum work obtainable from systems .

Combining eq.(21.26), $TdS - dq \geq 0$ and eq.(21.13), $dU = dq + dw$, we have, since $dq \leq TdS$

$$dU \leq TdS + dw \tag{21.33}$$

Rearranging,

$$dw \geq dU - TdS \tag{21.34}$$

The most negative value of dw is the maximum work dw_{max} obtained from the system;

$$dw_{max} = -dw$$

$$\text{or } dw = -dw_{max} \geq dU - TdS$$

$$\text{or } dw_{max} \leq -dU + TdS = -dA \tag{21.35}$$

at constant temperature. The maximum work that can be obtained from the system, dw_{max}, is equal to the decrease in the Helmholtz free energy of the system. Next, we want to consider the non-expansion work (i.e., work other than the pressure volume work such as electrical work) obtainable from the system. The total work done on the system dw is the sum of expansion work $-PdV$ plus any non expansion work w_{ne}

$$dw = -PdV + w_{ne} \tag{21.36}$$

For a constant temperature process from eq.(21.22),

$$dG = dH - TdS$$

Since $dH = dq + dw + d(PV)$ from equation eq.(21.9), we have

$$dG = dq - PdV + dw_{ne} + PdV + VdP - TdS \tag{21.37}$$

$$= dw_{ne} + VdP \tag{21.38}$$

At constant pressure,

$$dG = dw_{ne} \tag{21.39}$$

From eq.(21.39), we conclude that the work (other than pV work) obtainable from the system, $-dw_{ne}$ equals the decrease in the free energy dG. For a reversible process this is truly the maximum non PV work obtainable from the system, i.e.,

$$-dG = -(dw)_{ne, reversible} \tag{21.40}$$

In a chemical cell, the work performed by or obtainable from the cell $= n\,\varepsilon$ where n = no of moles electrons transferred during the process occurring at the electrode, F = Faraday = 96500 coulombs and ε of the cell. From eq.(21.40),

$$\triangle G = -n F\,\varepsilon \tag{21.41}$$

This will be used in our studies in electrochemistry.

21.12 Standard free energy changes for reactions

At each temperature, elements are in their standard states at 1 bar. Since the absolute value of the free energy of any element can not be determined, this standard value of free energy G^o in their most stable state is taken as zero. The

standard free energy of formation of a compound is the standard reaction free energy for the formation of the compound from its elements in their standard states. E.g., the standard reaction free energies $\triangle_r G^o$ for the following reactions at 298 K are

$$C + O_2 \rightleftharpoons CO_2, \ \triangle_r G^o = -394.4 \text{ kJ/mol}$$

$$\tfrac{1}{2} C + \tfrac{1}{2} O_2 \rightleftharpoons CO, \ \triangle_r G^o = -137.2 \text{ kJ/mol}. \tag{21.42}$$

The reaction free energies above are the standard free energies formation G^o_f for CO_2 and CO respectively.

The free energy changes for a reaction can be estimated from the free energies of formation of the reactants and products. Consider the following reaction,

$$CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g), \ (T = 298\ K) \tag{21.43}$$

For this reaction $\triangle_r G^o = -394.4 - 1/2\ G^o_f\ (O_2) - (-137.2) = -257.2 \text{ kJ/mol}$, since

$$G^o_f\ (O_2) = 0 \tag{21.44}$$

21.13 Pressure dependence of free energy.

At constant temperature, eq.(21.24) becomes

$$dG = VdP \tag{21.45}$$

and the free energy at pressure P_2, G_2 can be obtained through $G_2 - G_1 = \int_{P1}^{P2} VdP$

For an ideal gas, $V = nRT/P$ and $\qquad\qquad$ (21.46)

$$G_2 - G_1 = \triangle G = \int_{P1}^{P2} (nRT/P)\ dP$$

$$= nRT \ln (P_2 / P_1) \tag{21.47}$$

Free energy increases with increasing pressure, since volume is always positive.

Ex 21.4

Calculate the change in free energy when the pressure is increased from 1 atm to 10 atmospheres at 298 K for

- One mole of liquid water.The molar volume of water is 18 cc.and

- 1 mole of water vapour.

Solution

Let G^o be the free energy of the standard state at 298 K.

$G - G^o = \int_1^{200} VdP$ as the $- SdT$ term $= 0$ for constant T

$= 18\ (10-1)$, cc. atm assuming the molar volume to be independent of pressure. If the volume is given as

a function of pressure in a formula such as $V = V_0 + aP + bP^2$ where a and b are coefficients which depend on temperature, this form of V can be substituted in the above equation to get $\triangle G$ by integrating VdP.

For the vapour phase, assume ideal gas behaviour. For real gases, the actual equation of state is needed.

$\triangle G_{vapour} = VdP = nRT \ 1/P \ dP.$

$\qquad = nRT \ln (P_2 /P_1)$

$\qquad = 0.08206 \times 298 \ln 10 \ \text{lit atm.}$

$\qquad = 56.31 \ \text{lit atm .}$

21.14   **The equilibrium constant.**

For one mole of a gas A at any pressure P, the free energy is given by

$$G_A (p) = G^O_A + RT \ln P_A /P^O \qquad (21.48)$$

where P^O is the standard pressure of 1 bar and G^O_A is the standard free energy at 1 bar. When a reaction represented by the following equation takes place, (Ideal gas behaviour is assumed throughout this section).

$$aA + bB = cC + dD \qquad (21.49)$$

where, a, b, c and d are the stoichiometric coefficients, and reaches equilibrium, the initial pressures of A, B, C and D change to the final equilibrium values $(P_A)_{eq}$, $(P_B)_{eq}$, $(P_C)_{eq}$, $(P_D)_{eq}$. At equilibrium, the free energy has reached the lowest value and there will be no further decrease and so $\triangle G = 0$. The free energy change for eq.(21.49) can be written as

$\triangle G = G_{products} - G_{reactants}$

$$= c \ G_C + d \ G_D - aG_A - bG_B \qquad (21.50)$$

But $cG_C = cG^O_C + c \ RT \ln (P_C)_{eq} / P^O$ and similarly for A, B and D. Therefore,

$$\triangle G = \triangle G^0 + RT \{ \ln\{(P_c /P^0)^c (P_D /P^0)^d / (P_A /P^0)^a (P_B /P^0)^b \} \qquad (21.51)$$

Where $\triangle G^0 = c \ G^0_C + d \ G^0_D - a \ G^0_A - b \ G^0_B$. The ratio of pressures in eq (41.51) may be expressed as a factor Q.

$$\triangle G = \triangle G^0 + RT \ln Q \qquad (21.52)$$

At equilibrium $\triangle G = 0$, $Q = K_{eq}$ and we get

$\triangle G^O = - RT \ln K_{eq}$ where

$$K_{eq} = \{ (p_c /P^0)^c (P_D /P^0)^d /(P_A /P^0)^a (P_B /P^0)^b \}_{eq} \qquad (21.53)$$

Since P^0s are all equal to 1 bar,.they are left out in equations for K_{eq} with the understanding that P value will be treated as dimensionless (because of the implicit division by $P^0 = 1$bar).

Eq(21.52) is valid for ideal gases.For real gases, the pressures get replaced by effective pressures or fugacities f (which are defined by $RT \ln (f_2 /P) = {}_P \int^{P_2} VdP$ where f_2 is the fugacity at pressure P_2 . If the gas is ideal, $f_2 = P_2$) and for liquids and solids, they get replaced by activities a. The activity a is defined as relative fugacity, $a = f / f_o$, where f_o is the activity in a standard state. For example, if a solution is in equilibrium with its vapour, the chemical potentials or the fugacities of each component is the same in the liquid phase and the vapour phase. If the vapour pressure of say, component A is 400 mm Hg and the vapour pressure of its pure component (i.e., pure A) is 500 mm Hg, then the activity of the component A in the solution is 400/500 = 0.80. Here, we have assumed that the vapour behaves ideally and therefore, fugacities can be replaced by pressures. Fugacities and activities are central to all equilibrium constant estimations. Some of these aspects will be taken up in the chapter on electrochemical cells (Chapter 22).

Ex 21.5

For the reaction 2NH   N   +3H   the equilibrium partial pressures at 298 K are 0.9 bar, 0.1 bar and 0.2 bar

$3 \rightleftharpoons 2 \quad 2$
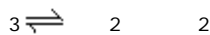
respectively for ammonia, nitrogen and hydrogen. Calculate K_{eq}. How does K_{eq} change with the total pressure on the system?

Solution

$K_{eq} = .1 \times (0.2)^3 / (0.9)^2$

$= 4.94 \times 10^{-3}$

K_{eq} is dimensionless. In the above calculation, each partial pressure is divided by the pressure in the standard state, P^0 which equals 1 bar for all gases and hence only the dimensionless numbers are given in the equation. If the total pressure of the system is changed, the partial pressures readjust to give the same K_{eq} as per the Le Chatelier's principle and K_{eq} remains unchanged, as it is determined by $\triangle G^0$, which is the difference in the standard state free energies at 1 bar. K_{eq} depends on temperature.

21.15 Problems

21.1) For 2 moles of a monatomic ideal gas, at 297.35 K and 1 atm, what is the volume of the system? For this fixed volume, if the temperature is doubled, what is the change in p, U and H? What are the values of q and w for this process? If this system is now compressed to half its volume at the constant system pressure, what is the work done on the system, $\triangle U$ and $\triangle H$? What is q for this process? In this state, the system has a temperature of 297.35 K. Now, the system undergoes an isothermal reversible expansion until it reaches the starting volume. Calculate w and q for this third step of this cycle. Represent this cyclic process on PV, VT and pT diagrams and calculate the changes in w, q, U and H for the cyclic process. For a constant volume process, $\triangle U = C_v \, dT$ and for constant pressure process, $\triangle H = C_p \, dT$. If $\triangle U$ is known, $\triangle H$ can be calculated as $\triangle H = \triangle U + \triangle (PV)$

21.2) The heat capacity of water C_P is 18 cal/(deg mol). What is the enthalpy change of water when it is heated from $25°C$ to $100°$ C? Assume C_P to be independent of temperature and use $\triangle H = C_P(T_2 - T_1)$. For the process $H_2O(l) \rightleftharpoons H_2O(s)$, $\triangle H\,(0\,°\,C) = -1436$ cal/mol. What is $\triangle H$ for this process at $-10°$ C? For ice, $C_P = 9$ cal/(deg mol). Use the Kirchoffs equation $\triangle H\,(T_2) = \triangle H(T_1) + \int_{T1}^{T2} \triangle C_P \, dT$. In this problem, assume C_P and $\triangle C_P$ to be independent of temperature.

21.3) The heat capacities of many substances can be expressed as $C_P = a + bT + cT^{-2}$ in the temperature range of 298 K to 2000 K. For CH_4, the values of the coefficients are a = 5.65, b = 11.44 x 10^{-3} and c = -7.0 x 10^5. The units (of C_P) are in cal/deg/mol. For CH_4, what is $\triangle H$ between 300 K and 1500 K? What would be $\triangle H$ if C was assumed to be a constant = 5.65 cal/(deg mol) in this temperature range?

21.4) What is the entropy change of the system in the following processes?

- Isothermal reversible expansion of an ideal gas from volume V_1 to V_2 at temperature T.

- Isothermal irreversible expansion of an ideal gas from V_1 to V_2.

- An adiabatic reversible expansion from V_1 to V_2.

- An adiabatic irreversible expansion from V_1 to V_2.

- A reversible cyclic process.

An irreversible cyclic process.

21.5) Freezing of water at $0°C$ is a reversible process because water and ice are in equilibrium at this temperature at 1 atm pressure. $\triangle H(0°C) = -1436$ cal/mol. What is the entropy change for this process? Here $\triangle H = q_{rev}$.

Liquid water can be supercooled below $0°C$. The supercooled liquid is unstable and can be easily frozen into ice, and the process not spontaneous. Calculate the entropy change in the spontaneous freezing of water at $-20°C$. Calculate the entropy change of the surroundings and $\triangle S_{universe}$. $\triangle S_{universe} = \triangle S_{system} + \triangle S_{surroundings}$.

Hint: Calculation of $<>\triangle S$ ca$<>$n not be done by dividing $q_{irr} = \triangle H (-20°C)$ by $T = 253K (= -20°C)$. Calculate $\triangle$ S in three reversible steps.

- $\triangle S_1$ = entropy change of water from 253K to 273K. $\triangle S = C_p \ln T_2 /T_1$, $C_p = 18$ cal/deg mol .

- $\triangle S_2$ = entropy of freezing at 273 K

- $\triangle S_3$ = entropy change of ice from 273 K to 253K. Use C_p (ice) = 9 cal/deg mol. To calculate $\triangle H_{surroundings}$, use $\triangle H_{surr} = - \triangle H_{sys}$, $\triangle H_{sys}$ (253K) = $\triangle H_{sys}$ (273K) + $\triangle C_p$ (T_2 -T_1). Assume $\triangle C_p$ to be independent of temperature. $\triangle C_p = C_p$ (ice) $- C_p$ (water).

21.6) One mole of an ideal gas is compressed from 1 atm to 100 atm at 350 K. What are the changes in the Gibbs free energy and the Helmholtz free energy?

21.7) At constant pressure dG = -SdT, and $(\partial G/\P T)_P$ = -S. Using the relation G = H -TS or S = (H-G)/T show that ∂ (G/T)/ $\P$ T = -H/T^2. This is called the Gibbs-Helmholtz equation. Applying this to changes in free energies in reactions, we get $[\partial (\triangle G/T)/ \partial T]P = - \triangle H / T^2$.

21.8) If $\triangle$is independent of T, the above equation can be integrated to give $\triangle \triangle G_1 / T_1 = \triangle H(1/T_2 - 1/T_1)$. The same formula can be applied for $\triangle G°$ as well . For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 298 K, $\triangle G° = \triangle G°_f = -3.97$ kcal/mol. Calculate K_{eq} using $\triangle G° = -RT \ln K_{eq}$ .If $\triangle H°f = -11.04$ kcal/mol for NH_3, and it is independent of temperature, calculate K_{eq} at 500 K.

21.9) In a gas phase reaction A + 2B $\rightleftharpoons$ 3C + 4D, 2 moles of A, 1 mol of B and 2 moles of D were mixed at 298K. When equilibrium was reached, the total pressure was 1 bar and the amount of C present was 0.3 moles. Calculate the equilibrium constant and the value of $\triangle G°$. First calculate the number of moles of all species at equilibrium.

21.10) Starting with dH = (∂ H/ ∂ T)$_P$ dT + (∂ H/ ∂ P)$_T$ dp, show that (∂ H/ ∂ P)$_T$ = - μ CP where $\mu = (\partial$ T/ ∂ P)$_H$. μ is the Joule Thompson coefficient. When μ > 0, gases cool on expansion. This principle is used in refrigeration.

21.11) Two containers A and B are placed next to each other. Both contain ideal gases at temperature T. The container A has volume V_A and n_A moles of A and container B has a volume V_B and n_B moles of B. When the partition between A and B is removed, both the gases mix and the entropy increases. Show that the entropy of mixing is - (n_A + n_B) [$x_A \ln x_A$ + $x_B \ln x_B$], where x_A and x_B are the mole fractions of A and B in the mixture.

Recap

In this Lecture you have learnt the following

Summary

In this chapter we distinguished between thermodynamic functions such as energy, entropy and free energies which depend on the state of the system alone and quantities such as work and heat, which depend on the path between two states of a system. The first two laws of thermodynamics give us the state functions energy and entropy.

The absolute value of entropy is given by the third law of thermodynamics. Since the absolute values of energy, enthalpy and free energy cannot be ascertained, standard states at each temperature are defined as the states at a pressure of 1 bar for each substance. Estimation of Δ U, Δ H, Δ A and Δ G were shown through examples. The criteria for spontaneous changes were obtained in terms of U, H, A and G and the maximum work obtainable from a system at constant temperature was shown to be - Δ A.

The maximum non pressure volume work such as nF ε was shown to be equal to - Δ G. Standard free energy changes were calculated for a few reactions. The dependence of free energy on pressure was estimated and the equilibrium constant was defined as the ratio of dimensionless pressures at equilibrium and this was related to the standard free energy change for the reaction.