CHAPTER II

METHODS OF ANALYSIS

Generally, Thermal Desorption Spectrometry involves, measurement of the rate of desorption from a surface as its temperature is increased in a programmed fashion. In this technique two heating schedules, a linear temperature sweep:

\[ T = T_0 + B \cdot t \]  \hspace{1cm} (1)

and a reciprocal temperature sweep,

\[ \frac{1}{T} = \frac{1}{T_0} - C \cdot t \]  \hspace{1cm} (2)

are employed.

where: \( T \) = Temperature of the sample in kelvin, at time \( t \) insec.

\( T_0 \) = Initial temperature (generally room temperature)

\( B \) and \( C \) are constants.

During these heating schedules, desorbing species are detected by a mass-spectrometer. Pressure change in the vacuum system during such heating schedules are governed by equation 3, developed by Redhead\(^{25}\) and Carter\(^{26}\)

\[ \frac{dP^*}{dt} + \frac{P^*}{T} = a \cdot N(t) \]  \hspace{1cm} (3)

where

\[ p^* = P - P_{eq} \]

\[ a = A/KV \]
and \[ \tau = \frac{V}{S} \]

\[ P = \text{Pressure at time } t \text{ in torr} \]

\[ P_{eq} = \text{Equilibrium pressure at time } t = 0 \text{, in torr.} \]

\[ A = \text{Area of sample in } \text{cm}^2. \]

\[ K = 3.27 \times 10^{19} \text{ molecule/liter at } p = 1 \text{ torr.} \]

\[ N(t) = \text{Desorption rate (molecules/cm}^2\text{.sec.)} \]

\[ V = \text{Volume of the system in litres.} \]

\[ S = \text{Pumping speed in liters/sec.} \]

\[ \tau = \text{Characteristic pumping time.} \]

It can be seen that for a large value of \( \tau \), i.e., large \( V \) and small \( S \), \( \frac{P^*}{\tau} \) term becomes negligible.

\[ N(t) = \frac{1}{a} \cdot \frac{dP^*}{dt} \]

Desorption rate is proportional to the rate of rise of pressure in this case.

Alternatively, for fast pumping speeds (\( \tau \rightarrow 0 \)) \( \frac{dP^*}{dt} \) term in the equation 3 becomes negligible.

\[ P^* = a \cdot \tau \cdot N(t) \]

Desorption rate is proportional to pressure in this case.

Based on equations 4 and 5, one can have two methods of obtaining thermal desorption spectra.

In the first method, one can either switch off the pump or isolate the pump from the system and start the programmed heating of the sample. During this heating schedule, a pressure signal
from the mass spectrometer can be electronically differentiated and plotted against time, to get the thermal desorption spectrum.

In the second method, one can have an appropriate pumping speed during the heating schedule. Pressure signal from the mass spectrometer in this case, is plotted against time, to get a desorption spectrum.

First method has been utilized in the present work because of its simplicity. In the second method one needs to take a number of trial spectra, till one attains suitable pumping speed to get a good desorption spectrum. Secondly one must know pumping speed corresponding to particular operating conditions used in the experiment. Solution to this problem is to have a conductance limited pumping. In order to avoid all these technical difficulties, first method was utilized in the present work.

Both the methods are based on the assumption that there is no readsorption of the desorbed species on the sample surface as well as on the system walls. This assumption is valid for ionically trapped inert gases. For chemisorbed gases, readsorption depends on the population of various desorbed phases, the pumping speed, sample temperature and time duration of the desorption cycle. The amount of readsorption is usually trivial, unless pumping speed is very low or desorption cycle is long.

The temperature at which the peak occurs in the desorption spectrum can be utilized to find out the activation energy of the desorption process associated with a particular peak.
Desorption process occurs via, zero, first or nth order kinetics. It may be a single or multiple step excitation process. Desorption process is generally of the first order in case of ionically entrapped inert gases. In case of entrapped gases desorption process is generally a multiple step excitation process in which during the first step, atom gets detrapped from the trapping site. Later, the detrapped atom diffuses upto the surface after multiple jumps.

Desorption rate from a unit surface area may be written as -

\[ N(t) \propto -\frac{d\Theta}{dt} = \nu_n \Theta^n \exp \left( -\frac{E}{kT} \right) \quad \ldots (6) \]

where, \( N(t) \) is the desorption rate (molecules/cm\(^2\).sec). \( E \) is the activation energy of desorption in eV, \( k \) is a Boltzmann constant in eV per kelvin. \( \Theta \) is the surface coverage in case of chemically active gases and number of trapped atoms in particular state in case of ionically trapped inert gases. \( n \) is the order of desorption reaction. \( n \) is the corresponding frequency factor. Redhead\(^{25}\) and Garter\(^{26}\) have derived following equations to relate peak temperature with activation energy.

\[ \frac{E}{kT_p^2} = \frac{\nu}{\Theta} \exp \left( -\frac{E}{kT_p} \right) \text{ for } n = 1 \quad \ldots (7) \]

where \( T_p \) is the peak temperature.

\[ \frac{E}{kT_p^2} = \frac{2 \nu \Theta_p}{\nu} \exp \left( -\frac{E}{kT_p} \right) \text{ for } n = 2 \quad \ldots (8) \]
where \( \Theta_p \) is the coverage at the peak temperature. Assuming appropriate value of the frequency factor, one can find the activation energy of first and second order desorption reactions.

Redhead\(^{25}\) has shown that, theoretical desorption transients for linear temperature sweep are given by following equations.

\[
\ln \left( \frac{N_p}{N} \right) = \frac{E}{k} \left( \frac{1}{T} - \frac{1}{T_p} \right) + \left( \frac{T}{T_p} \right)^2 \exp \left[ -\frac{E}{k} \left( \frac{1}{T} - \frac{1}{T_p} \right) \right] - 1 \quad \ldots (9)
\]

for \( n = 1 \)

where \( N_p \) is the desorption rate at peak temperature.

\[
\frac{N_p}{N} \approx \cosh^2 \left[ -\frac{E}{2k} \left( \frac{1}{T} - \frac{1}{T_p} \right) \right] \quad \text{for} \quad n = 2 \quad \ldots (10)
\]

Edwards and Kornelsen\(^2\) have shown that by using two heating rates \( B_1 \) and \( B_2 \) for linear heating schedules it is possible to find \( E \) without assuming a frequency factor by equation 9.

\[
\frac{E}{k} = \frac{T_p 1}{T_p 2} \frac{T_p 2}{T_p 1} \ln \frac{T_p 2}{T_p 1} \quad \text{for} \quad n = 1 \quad \ldots (11)
\]

Similar equation for second order reaction was developed in the present work. One can write equation 6, for two linear heating rates \( B_1 \) and \( B_2 \)

\[
\frac{E}{k T_p^2} = \frac{2 \nu}{T_{p1}} \exp \left( \frac{E}{k T_{p1}} \right) \quad \ldots (12)
\]

\[
\frac{E}{k T_p^2} = \frac{2 \nu}{T_{p2}} \frac{\Theta_p}{B_2} \quad \left( \frac{E}{k T_{p2}} \right) \quad \ldots (13)
\]
where $T_1$ and $T_2$ are peak temperatures. Simplifying these equations one can get the energy expression independent of frequency factor for second order description.

$$\frac{E}{k} = \frac{T_1 T_2}{T_2 - T_1} \cdot \ln \left( \frac{T_2^2 B_2 Q}{T_1^2 B_1 Q} \right)$$ \hspace{1cm} \text{(14)}

Similar equations have been derived in the present work for reciprocal heating schedules for two different heating rates $C_1$ and $C_2$. According to Redhead, relations between activation energy and peak temperatures for reciprocal heating schedules are following.

$$\exp \left( -\frac{E}{k T_p} \right) = \frac{C_1 E}{k \nu} \quad \text{for } n = 1$$ \hspace{2cm} \text{(15)}

and

$$\exp \left( -\frac{E}{k T_p} \right) = \frac{E}{2 \nu} \quad \text{for } n = 2$$ \hspace{2cm} \text{(16)}

Relation between $E$ and $T_p$, independent of frequency factor, for first order reaction was developed in the present work with the help of equation 13. Equation 13, for heating two rates $C_1$ and $C_2$ can be written as

$$\exp \left( -\frac{E}{k T_p} \right) = \frac{C_1 E}{k \nu}$$ \hspace{2cm} \text{(17)}

$$\exp \left( -\frac{E}{k T_p} \right) = \frac{C_2 E}{k \nu}$$ \hspace{2cm} \text{(18)}

Simplifying equations 15 and 16 we get the required relation as

$$\frac{E}{k} = \frac{T_1 T_2}{T_2 - T_1} \cdot \ln \left( \frac{C_1}{C_2} \right)$$ \hspace{1cm} \text{(19)}
Similar equation for second order reaction derived in the present work for reciprocal heating rates is

\[
\frac{E}{k} = \frac{T_p_1}{T_p - T_p_2} \ln \left( \frac{C_1}{C_2} \frac{\Theta_{p_2}}{\Theta_{p_1}} \right) \quad \ldots \quad (20)
\]

These expressions are useful if one wants to find the value of activation energy without assuming the frequency factor.

One can vary the heating rates in any of the heating schedules and measure the required parameters, to calculate the activation energy. To get accurate results it is necessary to get a measurable change in the parameters like peak temperatures and peak coverages. To get the measurable changes, it is necessary to change the heating rates at least by two orders of magnitude. One heating rate can be very slow and other can be very fast. Problems with the slow heating rate is that the electrodes surrounding the sample also can get heated up and start desorbing. That may create difficulties in the measurement of release rates. For fast heating rates, it is difficult to maintain linearity of the temperature sweep. Secondly, the recording system also has to be equally fast. These are some of the technical difficulties involved in this method. Besides, it is difficult to measure parameters like peak temperatures and surface coverages, if the peaks are overlapping or if there is considerable background desorption.

Various peaks in the desorption spectrum correspond to the possible binding states of the trapped gas atoms. Kornelsen has suggested that, peaks in the desorption spectra of entrapped inert
gases can be divided into two different groups $\alpha$ and $\beta$. The group of peaks correspond to single step desorption from sites very close to the solid surface. The $\alpha$ group of peaks correspond to desorption of atoms trapped at considerable depth below the surface layer. These atoms have to diffuse up to the surface before they are desorbed from the surface. $\alpha$ group of peaks have following properties.

1. Peak positions are independent of ion energies and direction of ion incidence.
2. Most of the $\alpha$ entrapment occurs in topmost few atomic layers.

$\beta$ peaks have following properties.

1. Peaks are observed for ion energies above certain threshold which depends on the type of ions, target material and direction of incidence in case of single crystals.

3. All the peaks are observed at higher temperatures compared to $\alpha$ group of peaks.
4. Peaks shift to higher temperature side with increase in the incident ion energy.
5. Peaks are wide compared to $\alpha$ peaks and are approximately symmetric about the peak position.
6. Peaks positions are sensitive to the direction of incidence in case of single crystals, because of channelling effects.
The properties mentioned above are consistent with desorption occurring via diffusive motion of gas in solids. Since active gases are generally adsorbed on the sample surface, a group of peaks are not expected.

It was established in the present work that positions of peaks also can change with incident ion energy, if the depth of trapping is within a layer of five to six atomic planes. Activation energy of desorption is governed by the depth of trapping site, from the surface.

Secondly, peaks may not be observed up to considerable incident ion energy if the activation energy of diffusion of the implanted gases is very small, as is the case with helium. Activation energy of interstitial diffusion of helium in molybdenum is ~ 0.3 eV. Therefore, one cannot expect much change in the effective activation energy of desorption with depth of the trapping site up to considerable depth.

Number of workers in this field have developed methods of analysing thermal desorption spectra. Redhead\textsuperscript{25} and Carter\textsuperscript{26} have done pioneering work in this area. Edwards\textsuperscript{36} has developed a method of estimating the activation energy of desorption without assuming a preexponential factor, with the help of width of peak. In another report\textsuperscript{37} he has estimated peak shifts in the desorption spectra due to vacuum time constants. Chan and Weinberg\textsuperscript{38} have found that for an accurate determination of activation energy and preexponential factor,
of first order desorption, the reciprocal of the product of heating rates and pumping time constant should be large, i.e. greater than 0.5 approximately. Chan et al. have also derived analytical expressions which allow determination of the activation energy of desorption and the preexponential factor using parameters such as peak temperature and peak width. Reed et al. have developed method of deconvolution of unresolved desorption spectra. Rood-bergen et al. have established that atoms detrapped from the trapping site and diffusing to the surface can get retrapped if they encounter a defect on their way to the surface. This process increases the effective activation energy of desorption leading to peak-shifts to the higher temperature side. Edwards Jr. and Kornelsen have established that most accurate method to get \(E\) and independently is to combine linear temperature sweep and constant temperature - anneal method. Donnelly et al. have derived release transient, when activation energies have Gaussian distribution. Schmidt, King and Ehrlich have reviewed methods of analysing desorption spectra.