ABSTRACT
When molecules or atoms come in contact with a surface, they adsorb onto it, minimizing their energy by forming a bond with the surface. The binding energy varies with the combination of the adsorbate and surface. If the surface is heated, at one point, the energy transferred to the adsorbed species will cause it to desorb. The temperature at which this happens is known as the desorption temperature. Thus TDS shows information on the binding energy. In particular, the spectral peak widths and the temperature at which the maximum rate of desorption occurs may be used to describe both first-and second-order desorption kinetics. An explicit application of this method in the analysis of several important classes of desorption reactions is presented.

KEYWORDS: Thermal desorption spectroscopy, quadrupole mass spectrometer, ultra vacuum chamber.

INTRODUCTION
When matter is heated it undergoes certain physical and chemical changes. These physical and chemical changes take place over a wide temperature range. Physical changes such as melting and boiling may occur at widely varying temperatures, depending on the material involved. Chemical changes, such as decomposition or reaction, may also take place at very different temperatures.

The physical and chemical changes a sample undergoes when heated, are characteristic of the material being examined. By measuring the temperature at which such reactions occurs and the heat involved in the reaction, we can characterize the compounds present in the material. The physical and chemical changes that take place when unknown sample is heated provide us with information that enables us to identify the material.
Thermal desorption mass spectroscopy (TDS), also known as temperature programmed desorption (TPD) is the method of observing desorbed molecules from surface when the surface temperature is increased. Thermal desorption mass spectroscopy (TDS) techniques are important methods for the determination of kinetic and thermodynamic parameters of desorption processes or decomposition reactions. A sample is heated with a temperature program \( \beta(t) = dT/dt \) (with the temperature T usually being a linear function of the time t) and the partial pressures of atoms and molecules evolving from the sample are measured, e.g. by mass spectrometry. When experiments are performed using well-defined surfaces of single-crystalline samples in a continuously pumped ultra-high vacuum (UHV) chamber then experimental technique is referred as thermal desorption mass spectroscopy (TDS).

**DESORPTION**

The term “desorption” is defined as when molecules or atoms come in contact with a surface, they adsorb onto it, minimizing their energy by forming a bond with the surface. The binding energy varies with the combination of the adsorbate and surface. If the surface is heated, at one point, the energy transferred to the adsorbed species will cause it to desorb. The temperature at which this happens is known as the desorption temperature. Thus TDS shows information on the binding energy. A mass spectrometer is used for the detector generally. We use a quadrupole mass spectrometer as the detector in our TDS instrument. The thermal desorption curve that has X-axis as the temperature and Y-axis as the ion intensity as shown in figure 1 is provided with this composition. One thermal desorption curve at every mass number is porovided.

**DESORPTION MEASUREMENT**

Since TDS observes the mass of desorbed molecules, it shows what molecules are adsorbed on the surface. Moreover, TDS recognizes the different adsorption conditions of the same molecules from the differences between the desorption temperatures of molecules desorbing different sites at the surface, e.g. terraces vs. steps. TDS also obtains the amounts of adsorbed molecules on the surface from the intensity of the peaks of the TDS spectrum, and the total amount of adsorbed species is shown by the integral of the spectrum.
To measure TDS, one needs a mass spectrometer, such as a quadrupole mass spectrometer or a time-of-flight (TOF) mass spectrometer, under ultra vacuum (UHV) conditions. The amount of adsorbed molecules is measured by increasing the temperature at a heating rate of typically 2k/s to 10k/s. Several masses may be simultaneously measured by mass spectrometer, and the intensity of each mass as a function of temperature is obtained as a TDS spectrum. The heating procedure is often controlled by the PID control algorithm, with the controller being either a computer or specialized equipment such as a Eurotherm.

Two kinds of the measurement method with the mass spectrometer show different data.

1. MID (Multi Ion Detection) data.
2. Scan data

Other methods of measuring desorption are Thermal Gravimetric Analysis (TGA) or using infrared detectors, thermal conductivity detectors etc.

**PRINCIPLE**

In principle can get

- Heat of adsorption (if adsorption and desorption are reversible/non dissociate processes)
Fig:2 conventional Lennard-Jones picture of dissociative adsorption

of a diatomic molecule AB on surface: (a) non-activated (b) activated for (a) \( E_{ads} = E_{des} \) but for (b) \( E_{ads} < E_{des} \).

- Quantitative coverage information about dissociative and non-dissociative Adsorption
- Energetic information about phases transitions, inter adsorbate interactions, multiple adsorption sites.\(^2\)
- Kinetic information about desorption process.

**Two ways to collect data**

(a) thermal desorption (TPD/TDS)
- rate of desorption < pumping speed of vacuum system
- most common method

(b) flash desorption
- rate of desorption > pumping speed of vacuum system
- rarely used.
Partial pressure recorded at one m/z (say, base peak) by mass spectrometer is:

- $\infty$ to instantaneous partial pressure of adsorbate $P^M$
- $\infty$ to rate of desorption of adsorbate $\frac{dM}{dT}$
- $\frac{dM}{dT}$=rate of loss of coverage

Several points worth noting:

- $I(T)$ does not rise indefinitely - at some stage, all molecules desorbed
- If the mass spectrometer collected and ionized all adsorbates, area under TDS $I(T)$ curve would equal molecular coverage $\frac{dy}{dx}$
- Only fraction desorbed molecules collected and ionized-area under TDS $I(T)$ curve is proportional to molecular coverage.
- Shape of $I(T)$ curve contains information about desorption kinetics.
The theoretical description of TDS data

The rate of desorption follows Arrhenius-type behavior

\[ I(T) \propto \frac{dM}{dt} = -\frac{d \Theta_M}{dt} = \nu(\Theta_M) \cdot \Theta_M^n \cdot \exp \left( \frac{-E_{\text{des}}(\Theta_M)}{R \cdot T} \right) \]

Where:

\( n(\Theta_M) \) = frequency factor

\( \Theta_M \) = instantaneous coverage

\( n \) = kinetic order or desorption order

\( E_{\text{des}}(\Theta_M) \) = activation energy to desorption

\( R \) = gas constant

During TDS sample is heated in linear fashion

\[ T(t) = T_0 + \frac{dT}{dt} \cdot t = T_0 + \beta t \]

where \( \beta \) is the heating rate (K·s\(^{-1}\))

Polanyi-Wigner equation becomes:

\[ -\frac{d \Theta_M}{dT} = \frac{\nu \cdot \Theta_M^n}{\beta} \cdot \exp \left( \frac{-E_{\text{des}}}{R \cdot T} \right) \]

The rate contains a coverage term \( (\Theta_M^n) \) and energy term:

- At low T, \( E_{\text{des}} > RT \) and little desorption occurs - \( I(T) \sim 0 \)
- At high T, \( \exp(\frac{-E_{\text{des}}}{RT}) \) rises rapidly - \( I(T) > 0 \)
• As coverage decreases following desorption of fraction of monolayer, I(T) decreases
• At very high T, all molecules desorbed - I(T) = 0

Significance of Desorption Order (n)
Most terms in Polanyi-Wigner equation straightforward
• Factors affecting peak desorption temperature:
  - $E_{des}$, $n$, $\beta$, $\theta_m (n \neq 1)$
• Factors affecting peak shape:
  - $n$, $b$, $n$
• Factors affecting peak magnitude (area):
  $\theta_m$
What about desorption order n?

Zero-order desorption kinetics

$$-\frac{d\theta_M}{dt} = v \cdot \theta_M n=0 \cdot \exp \left( \frac{-E_{des}}{R \cdot T} \right)$$

• implies that desorption rate does not depend on coverage
• implies that desorption rate increases exponentially with T - all coverages have common leading edge
• rapid drop when all molecules have desorbed
• temperature of peak desorption rate, $T_m$, moves to higher T with $q_m$
• Zero-order kinetics observed in thick layers (multi layers) when supply of Molecules is ~ infinite

May also occur if strong attractive interactions between adsorbates (pseudo zero-order)\(^3\)
**First-order desorption kinetics**

\[-\frac{d\theta_M}{dt} = v \cdot \theta_M \cdot \exp\left(\frac{-E_{des}}{R \cdot T}\right)\]

- desorption rate proportional to instantaneous coverage
- desorption peak will show balance of $q_M$ and $\exp(-E_{des}/RT)$ terms
  - $T_m$ constant with increasing $q_m$
- characteristic asymmetric peak shape
- $T_m$ increases with $E_{des}$
- "Normal" desorption order for non-dissociative molecular and atomic adsorption.

**Second-order desorption kinetics**

\[-\frac{d\theta_M}{dt} = v \cdot \theta_M^2 \cdot \exp\left(\frac{-E_{des}}{R \cdot T}\right)\]

- desorption rate proportional to instantaneous coverage\(^2\)
- desorption peak will show balance of $q_M$ and $\exp(-E_{des}/RT)$ terms
- Common trailing edges of peaks
- Characteristic nearly symmetric peak shape

**Fractional-order desorption kinetics:**

Occasionally fractional order ($0 < n < 1$) desorption is observed

- believed to indicate cluster formation on surface
- desorption from edges of cluster (2-D or 3-D)

**Quantitative Interpretation of TDS data**

TDS spectrum 1 and 2 are typical examples of a TDS measurement. Both TDS are examples of NO desorbing from a single crystal in high vacuum. The crystal was mounted on a titanium filament and heated with current. The desorbing NO was measured using a mass spectrometer monitoring the atomic mass of 30.

Before 1990 analysis of a TDS spectrum was usually done using a so-called simplified method; the "Redhead" method, assuming the exponential pre factor and the desorption energy to be independent of the surface coverage. After 1990 and with use of computer algorithms TDS spectra were analyzed using the "complete analysis method" or the "leading
edge method”. These methods assume the exponential pre factor and the desorption energy to be dependent of the surface coverage.[4]

Fig:4 TDS Spectrum 1 A Thermal Desorption Spectrum of NO absorbed on Platinum-Rhodium (100) single crystal. The unit of the x-axis is temperature in Kelvin, the unit of the y-axis is an arbitrary unit, in fact the intensity of a mass spectrometer measurement.

Fig:5 TDS Spectrum 2 A Thermal Desorption Spectrum of NO absorbed on Platinum-Rhodium (100) single crystal. The spectra of several NO coverages are combined in one spectrum. The unit of the x-axis is temperature in Kelvin, the unit of the y-axis is an arbitrary unit, in fact the intensity of a mass spectrometer measurement.

INSTRUMENTATION
a. Ultra vacuum(UHV) Chamber
The UHV system consists of a pumping system and the vacuum vessel. All parts of the vacuum vessel are made from high-grade steel. All mountable parts are attached using standard Conflat flanges, which have a knife edge that affords a seal by cutting into an oxygen-free high-conductivity (OFHC) copper ring ("gasket"). Besides the pressure gauge described above, the following equipment is attached to the chamber and will be utilised for the experiment.
A leak valve, allowing the controlled dosing of gases into the UHV chamber.
A manipulator onto which a sample can be mounted for studies of its surface properties.
An ion gun, used for cleaning the surface of the sample by bombardment with ions accelerated to kinetic energies of approximately 1 keV ("sputtering").
A quadrupole mass spectrometer.

Fig:6  The ultrahigh vacuum apparatus used for this experiment.

b. Vacuum generation and pumping speed
Vacuum is maintained by a turbomolecular pump ("turbo") backed by a rotary oil pump. A turbo molecular pump consists of a cylindrical case with stator blades and rotor blades turning at very high speeds (typically in the range of 50,000–rotations/min.). If a gas particle from the Vacuum chamber enters the inlet of the pump it collides with a rotor blade and its momentum vector is changed towards the outlet of the pump. It is then removed from the vacuum vessel by a succession of such collision events until it reaches the outlet of the turbomolecular pump. There it encounters the suction action of a rotary pump that maintains a pressure of approximately $10^3$ mbar.$^{[5]}$
C. Pressure Measurement

In the ultra-high and high vacuum ranges (up to approximately 0.001 mbar), the pressure is most conveniently and accurately measured by means of a Bayard-Alpert ionisation gauge. It consists of a glowing filament, a grid cage (anode) and the target electrode (cathode). The filament is made of tungsten wire and is resistively heated to a temperature above 2500°C (white heat). At this temperature electrons are emitted, which ionise gas particles in the environment of the filament. The cations generated by this process are accelerated into the grid cage where they are collected by a target electrode biased at a potential of approximately 600V. The resulting ion current at the collector is a measure of the pressure. Quantitatively, the pressure $p$ depends on the ion current $I_c$ at the collector and the emission current $I_{em}$ of the filament according to

$$I_c = S \cdot p \cdot I_{em}$$

Here, the sensitivity $S$ [mbar$^{-1}$] is a quantity that depends on the gas and the apparatus used. It is tabulated for common gases. For pressures exceeding 10-3 mbar other types of pressure gauges must be employed: most of these are based on the measurement of the resistance of a thin wire (Pirani gauges), which depends on the heat conductivity of the medium in its
environment. The better the vacuum around the wire the lower the heat conductivity of the environment, resulting in a warmer wire with a higher resistance. A variation of this principle is the thermocouple gauge. It is based on a measurement of the thermo voltage at a metal-metal junction, which also depends on the heat conductivity of its surroundings.

d. Dosing of Gases
Dosing of gases into the chamber is achieved by use of a leak valve. The final pressure pf measured during dosing is the sum of the base pressure p0 and the partial pressure pi of the gas flowing into the system, i.e., pf - p0 = pi (or pi = pf for p0 << pf). The partial pressure pi is proportional to the particle number ni. In UHV studies of adsorption the unit Langmuir (1 L = 10^-6 torr s) is used to describe the amount of gas dosed into the system, i.e., 1 L is the gas dose that corresponds to a pressure increase to 10^-6 torr (760 torr = 101.325 kPa) for 1 s. The number of gas-surface collisions during such a pressure burst is of the same order of magnitude as the number of surface atoms. (6)

e. Sample Manipulation and Mounting
The sample manipulator is based on a rotatable rod that can be moved horizontally (x,y-plane) and vertically along its z-axis. The manipulator also has electrical feed throughs with ceramic insulation for connecting crystal mounting wires to a power supply for resistive heating and two thermocouple wires to a temperature controller. A sketch of the manipulator assembly is given in Figure 8. Movement of the manipulator rod is possible through use of special vacuum-tight bellows that are made from stainless steel. Micrometer screws allow the accurate positioning of the crystal.

The sample is mounted on 0.2 mm – 0.4 mm diameter W- or Ta-wires that are supported by Cu-rods, the top of which is attached to a ceramic block. Use of the ceramic block affords Electrical insulation of the Cu rods, so that high currents (max. 40 A) can be passed through them to heat the mounting wires resistively. Temperatures of up to approximately 1700 K can thus be obtained at the single crystal sample. The heating power is regulated by a temperature controller that reads the voltage of a thermocouple welded to the side of the single crystal sample.
f. Sample Preparation

The sample is not only subjected to contamination by interaction with particles in the background pressure of the vacuum chamber, but also by segregation of crystal impurities. Particularly troublesome are usually non-metallic contaminants in the crystal lattice, such as carbon, oxygen and sulphur. While contaminants from the gas phase can often be removed by gentle heating of the sample, segregated contaminants must often be removed by a different method. Often used are so-called sputter-heat cycles: the carbidic, oxidic or sulphidic contaminants at the surface are first removed by bombardment of the surface with ions (Ne+, Ar+ or Kr+ are the most common choice) accelerated to kinetic energies between 500 eV and 2000 eV. On impact with the sample surface the momentum of the ions is transferred to lattice vibrations in the surface region. This leads to the breaking of bonds to and between surface atoms and the removal of surface atoms layer-by-layer.⁷

g. QUADRUPOLE MASS SPECTROMETER (QMS)

The QMS consists of three components:

(i) the ion source with electron impact ioniser and ion extraction optics.

(ii) the actual quadrupole analyser consisting of four cylindrically rods.

(iii) the ion detector (electron multiplier).
In the present experiment, the ions are generated by electron impact ionisation (as in most conventional mass spectrometers). Free electrons are formed by thermal emission from an electrically heated tungsten filament. Thermal electron emission can be described by the Richardson-Dushman equation

\[ J = C \cdot \exp \left( -\frac{\Phi}{kT} \right) \]

with \( J \) the current density of emitted electrons, \( C \) a constant (independent of the filament material), \( T \) the temperature and the work function of the filament material. It is intuitive to see that the emission current increases with the temperature.

The emitted electrons are accelerated by a potential difference (typically 70 V) between the filament and the grid (Figure 5). Ionisation takes place in the area between grid and aperture, which are at approximately equal potentials. The temperature of the filament is in the range around 2500 K. The emitted electrons have a certain kinetic energy distribution due to the temperature of the filament, but also (more important) due to the electrical potential drop across the heated filament. The energy distribution is typically in the range 2 eV.

![Parts of a quadrupole mass spectrometer.](image)

The quadruple analyser consists of four cylindrical rods, arranged symmetrically at a distance \( r_0(x, y) \) around the optical axis \( z \) of the system. Opposite rods are electrically connected\(^{(8)}\). The Voltage applied to the two pairs of opposite rods can be expressed as

\[ V_1 = U + V \cdot \cos(\omega \cdot t) \]
\[ V_2 = -(U + V \cdot \cos(\omega \cdot t)) \]
With a constant component $U$ and a radiofrequency component $V \cdot \cos(\omega \cdot t)$.

In the $(x,y)$-plane (perpendicular to the quadrupole axis) the potential at any point between the rods is

$$\Phi(x,y) = \frac{(U + V \cdot \cos(\omega \cdot t)) \cdot (x^2 - y^2)}{r_0^2}$$

The differential equations of motion for an ion in such a potential are known as Mathieu equations. Their analysis reveals that for a given ion ($m/Ze$) only certain values of $U$ and $V$ result in stable oscillatory trajectories, while for other values for $U$ and $V$ the amplitude of the oscillations increases exponentially, so that the ion will strike a rod and lose its charge.\[10\]

Note that particles are separated according to their mass/charge ratio $m/Ze$; doubly ionized particles thus appear in the spectrum at half their molecular mass, triply charged ions at one third, etc. By this method, molecules with molecular masses of over 1000 can be detected even if the mass spectrometer has a maximum range of, e.g., 300 amu. Apart from the isotope pattern of the molecular ion one can also observe products of ion fragmentation processes.

The simplest way of detecting ions or electrons is via the detection of their charges. In simple Quadrupole mass spectrometers the ions hit a metallic collector cone (Faraday cup) and the charge transferred is recorded using an electrometer preamplifier, which can detect currents down to the pA-range. For even lower ion currents (i.e., for less than 10$^7$ ions per second), one uses secondary electron multipliers or channeltron multipliers. Interpretation of Thermal Desorption Spectra.\[9\]

**Instructions for the Experiment**

• Examine the apparatus and identify the various devices attached to it. Convince yourself that the pressure in the chamber is in the 10$^{-9}$ mbar range or lower.
• Clean the single crystal surface in the chamber by two cycles of 30 min Ar$^+$-sputtering followed by heating the crystal to restore surface order (the instructor will provide you with exact conditions for these procedures).\[10\]
• Collect TDS spectra for a CO dose of 0.5 L as a function of the heating rate. Use heating rates of 20 K/s, 10 K/s, 5 K/s, 1 K/s and 0.5 K/s. Analyse the results with the method described in section 2.9.
• Collect a series of TDS spectra for the following doses of CO (complete the table below before you start the experiments!). Use a heating rate of 5 K/s. Repeat the experiments for gas doses of 0.06 L, 0.36 L and 1.00 L so that you can estimate the experimental error.

**Tabel:1: A series of TDS spectra for the different doses.**

<table>
<thead>
<tr>
<th>Dose [L]</th>
<th>0.03</th>
<th>0.06</th>
<th>0.09</th>
<th>0.18</th>
<th>0.27</th>
<th>0.36</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
<th>1.50</th>
<th>2.00</th>
<th>5.00</th>
</tr>
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<tr>
<td>Dosing Tim [T]</td>
<td>6</td>
<td>12</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Pressure [torr]</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-8})</td>
<td>5.10(^{-8})</td>
<td>5.10(^{-7})</td>
<td>1.10(^{-7})</td>
<td>1.10(^{-7})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure [Mbar]</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-9})</td>
<td>5.10(^{-8})</td>
<td>5.10(^{-8})</td>
<td>5.10(^{-7})</td>
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<td>1.10(^{-7})</td>
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</tbody>
</table>

• Determine activation energies and pre exponential factors for this series using the analysis methods described in sections 2.10 and 2.12. Compare and discuss the results.

**ADVANTAGES:**

- Fastest MS analyzer.
- It is simplicity and ruggedness.

**DISADVANTAGES**

- Binding sites occupied at low temperature not necessarily those from which molecule desorbs during TDS.
- Mathematical treatment of data useful but can be easily misapplied.
- Often very complex desorption kinetics observed even for \(-n\), \(Edes\), \(n\) are temperature dependant.
- Difficult to determine temperature of reaction.
- Fragments with coincident m/z peaks can complicate interpretation.

**APPLICATIONS**

1. TDS application in quantitative studies of hydrogen trapping and release behavior in different crystalline and non-crystalline materials.
2. To the study of defects induced by arsenic implantation.
3. The defects induced by through-oxide implantation of arsenic into silicon have been studied using the TDS after hydrogen adsorption on the defects.
4. The thermal decomposition of alane was investigated by application of synchrotron x-ray diffraction and TDS.
5. To study the metallo fullerene primary soots by TDS. For a large variety of alkaline earth and lanthanide elements.\(^{[11]}\)
6. TDS involves heating a sample under UHV conditions and simultaneously measuring a number of desorbing gas species as a function of sample temperature.

CONCLUSION

➤ Simple, rapid
➤ Quantitative coverage information (simplest case)
➤ Can accurately determine exposure required for 1 ML coverage (in layer-by-layer systems)
➤ Provides information about adsorption/desorption enthalpies (simplest non dissociative case)
➤ Provides information about layer stability

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