

Desorption techniques

- Thermal Desorption Spectroscopy (TDS)
- Electron Stimulated Desorption (ESD)
- Electron Stimulated Desorption Ion Angular Distribution (ESDIAD)
- Photon Stimulated Desorption (PSD)

Thermal desorption spectroscopy (TDS) or Temperature Programmed Desorption (TPD)

Adsorbed molecule bound to surface in potential well of depth E_{des}

Probability that molecule will desorb at any one temperature, to produce an equilibrium vapor pressure, is governed by Boltzmann statistics

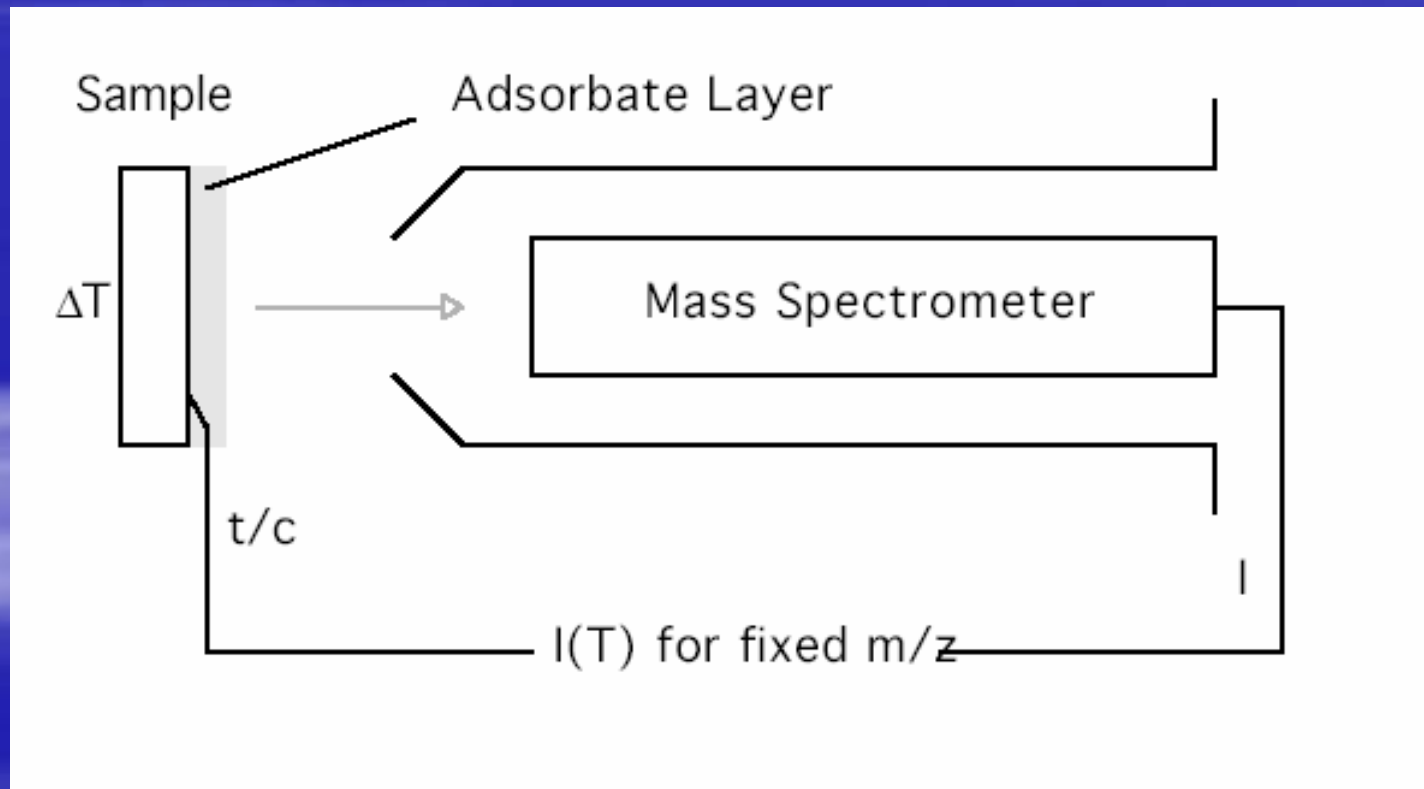
In TPD experiment, gaseous molecule/atom is adsorbed onto surface (sometimes cooled) then desorbed by heating surface

Pressure rise monitored by

- total pressure gauge (e.g. ion gauge)
- mass spectrometer

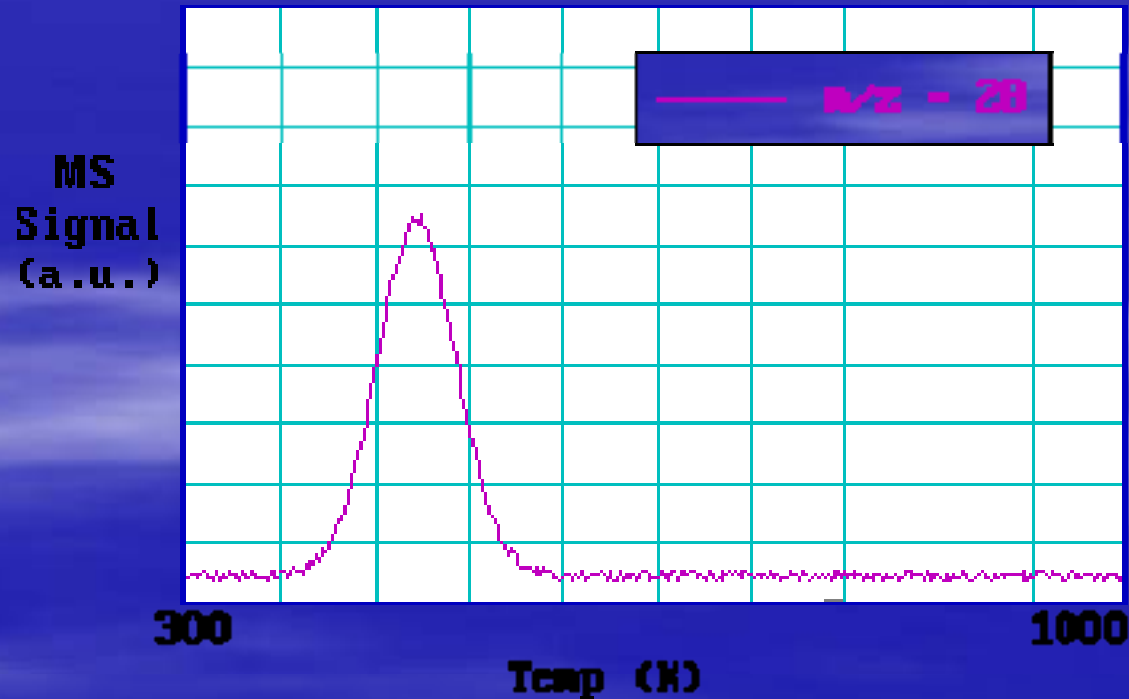
usually quadrupole (not TOF)

can acquire single or multiple m/z during heating



The data obtained from such an experiment consists of the intensity variation of each recorded mass fragment as a function of time / temperature. In the case of a simple reversible adsorption process it may only be necessary to record one signal - that attributable to the molecular ion of the adsorbate concerned.

The graph below shows data from a TPD experiment following adsorption of CO onto a Pd(111) crystal at 300 K.



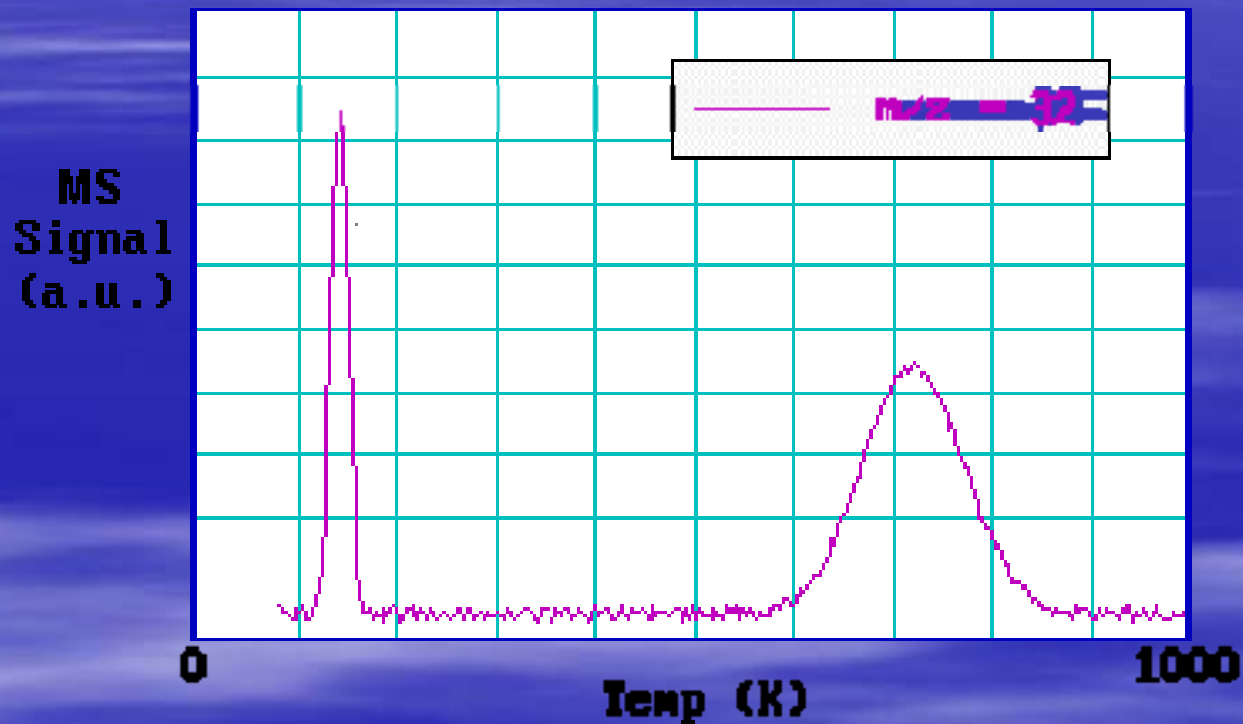
The area under a peak is proportional to the amount originally adsorbed, i.e. proportional to the surface coverage.

The kinetics of desorption (obtained from the peak profile and the coverage dependence of the desorption characteristics) give information on the state of aggregation of the adsorbed species e.g. molecular v's dissociative.

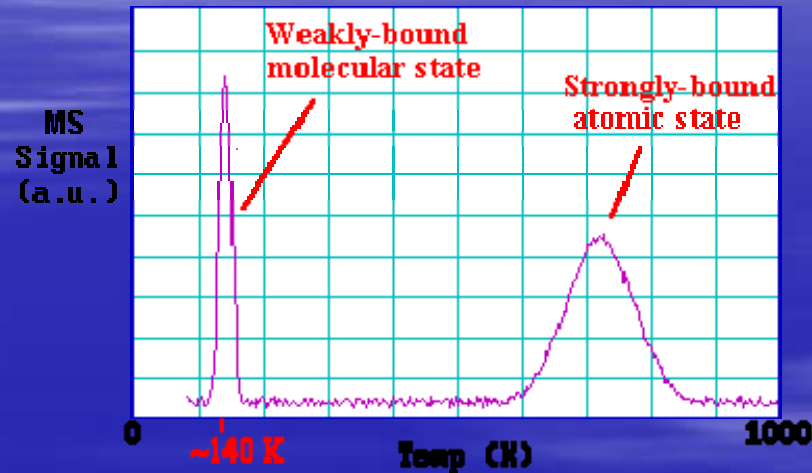
The position of the peak (the *peak temperature*) is related to the enthalpy of adsorption, i.e. to the strength of binding to the surface.

One implication of the last point, is that if there is more than one binding state for a molecule on a surface (and these have significantly different adsorption enthalpies) then this will give rise to multiple peaks in the TPD spectrum.

The graph below shows data from a TPD experiment following adsorption of oxygen on Pt(111) at 80 K.



The peak at ca. 140 K corresponds to desorption of the more weakly bound state



The more weakly bound state has the lower activation energy for desorption and will therefore undergo desorption at a lower temperature. The two peaks correspond to the presence of both molecularly and atomically (i.e. dissociatively) adsorbed oxygen on the surface.

The molecular species is the more weakly adsorbed.

One can obtain:

- Heat of adsorption (if adsorption and desorption are reversible/nondissociative processes)
- Quantitative coverage information about dissociative and nondissociative adsorption
- Energetic information about phases transitions, interadsorbate interactions, multiple adsorption sites
- Kinetic information about desorption process

Partial pressure recorded at one m/z (say, base peak) by mass spectrometer is

- \propto to instantaneous partial pressure of adsorbate p_M
- \propto to rate of desorption of adsorbate $\frac{dM}{dt}$
- $\frac{dM}{dt} = \text{rate of loss of coverage} = -\frac{d\theta_M}{dt}$

- $I(T)$ does not rise indefinitely - at some stage, all molecules desorbed
- If the mass spectrometer collected and ionized all adsorbates, area under TPD $I(T)$ curve would *equal* molecular coverage
- Only fraction desorbed molecules collected and ionized – area under TPD $I(T)$ curve is *proportional* to molecular coverage
- Shape of $I(T)$ curve contains information about desorption kinetics

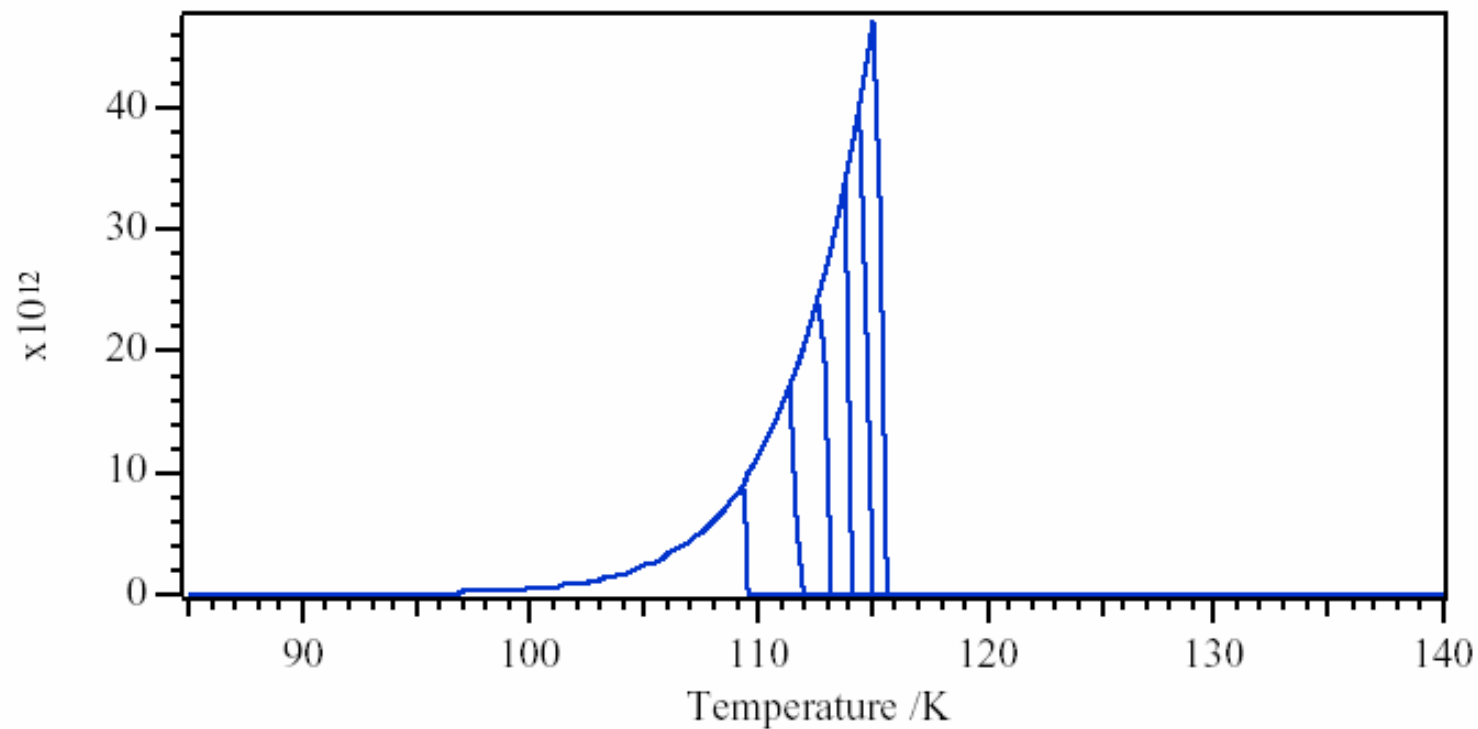
Zero-order desorption kinetics:

$$\begin{aligned} -\frac{d\theta_M}{dt} &= v \cdot \theta_M^{n=0} \cdot \exp\left(\frac{-E_{\text{des}}}{R \cdot T}\right) \\ &= v \cdot \exp\left(\frac{-E_{\text{des}}}{R \cdot T}\right) \end{aligned}$$

implies that desorption rate does not depend on coverage

implies that desorption rate increases exponentially with T

Zero Order TPD: $E_d=30$ kJ/mol $\nu=1 \times 10^{28}$ $\beta=1.5$ K/s $\Theta_M=1-6 \times 10^{13}$ cm⁻²



- 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 θ_m

Zero-order kinetics observed in thick layers (multilayers) when supply of molecules is \sim infinite

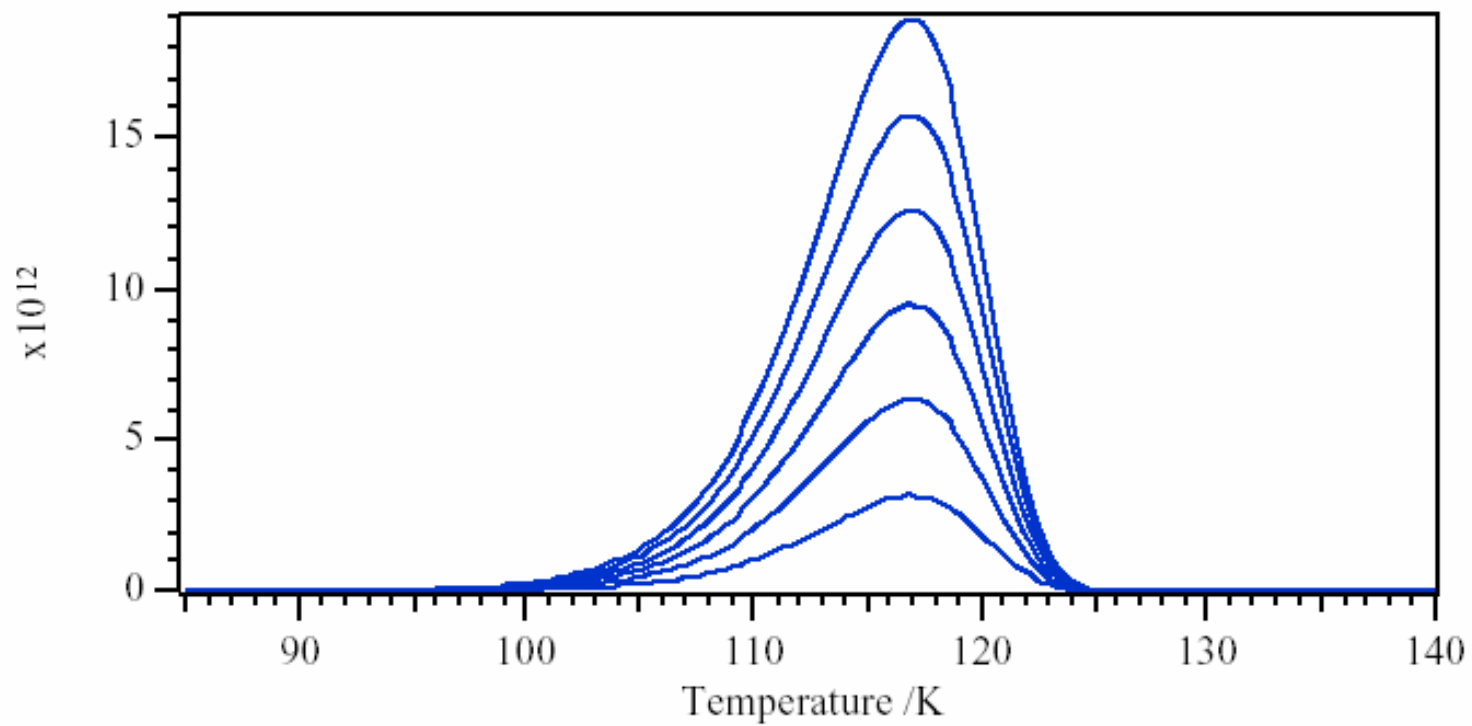
May also occur if strong attractive interactions between adsorbates (*pseudo* zero-order)

First-order desorption kinetics

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

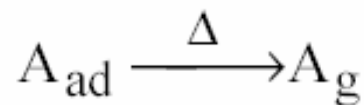
- desorption rate proportional to instantaneous coverage
- desorption peak will show balance of θ_M and $\exp(-E_{des}/RT)$ terms

First Order TPD: $E_d=30$ kJ/mol $v=1 \times 10^{13}$ $\beta=1.5$ K/s $\theta_m=1-6 \times 10^{13}$ cm⁻²



- T_m constant with increasing θ_m
- characteristic asymmetric peak shape
- T_m increases with E_{des}

"Normal" desorption order for non-dissociative molecular and atomic adsorption

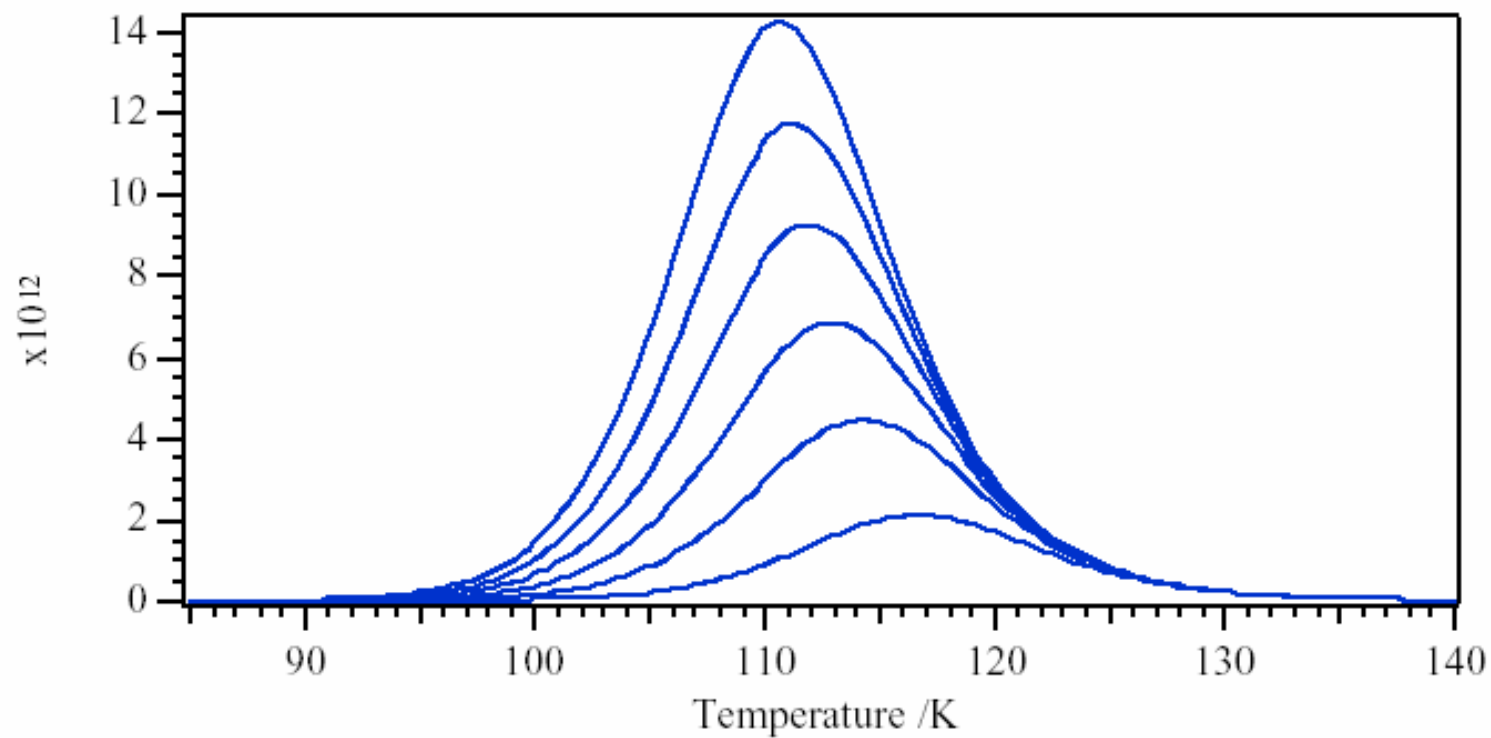


Second-order desorption kinetics:

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

- desorption rate proportional to instantaneous coverage²
- desorption peak will show balance of θ_m and $\exp(-E_{\text{des}}/RT)$ terms

Second Order TPD: $E_d=30$ kJ/mol $\nu=1 \times 10^{-1}$ $\beta=1.5$ K/s $\theta_m=1-6 \times 10^{13}$ cm $^{-2}$



- T_m moves to lower T with θ_m
- Common trailing edges of peaks
- Characteristic nearly symmetric peak shape

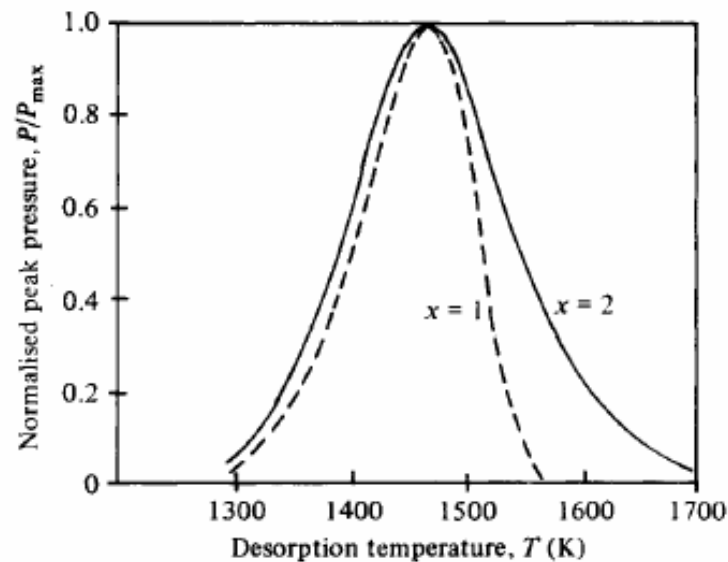
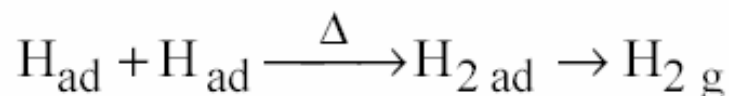


Fig. 5.6 The theoretical shapes of first- and second-order desorption peaks (Redhead, 1962).

For hydrogen on W, β_2 peak shows second-order desorption kinetics



Pseudo second-order desorption observed for strong *repulsive* interadsorbate interactions

- repulsion increases with coverage and so lowers average desorption temperature

- $$-\frac{d\theta_M}{dt} = v \cdot \theta_M^2 \cdot \exp\left(\frac{-E_{des} + (a \cdot \theta_M \cdot E_{repulsion})}{R \cdot T}\right)$$

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)