

# Measuring Adsorption Enthalpies by Microcalorimetry -An Introduction of Single-crystal Adsorption Calorimeter

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## 1. INTRODUCTION

The heat of adsorption of a given adsorption process is one of the most useful parameters in surface science studies. Despite the enormous body of data that has been obtained using modern surface science techniques over the past forty years, however, it was often not clear what the adsorbates being formed on such films really were, or which of the many different sites on its heterogeneous surface were populated. With the recent development of David King's group at Cambridge University of a new apparatus, single-crystal adsorption calorimeter (SCAC) is capable of measuring heats of adsorption of gases as a function of coverage on single crystal metal films of controlled cleanliness over a wide range of temperatures, by using a pulsed molecular beam source for gas dosing and a photoconductive<sup>[1]</sup> or pyroelectric temperature sensor<sup>[2]</sup>. It is possible to accurately measure calorimetric adsorption heats on single-crystal surface for many types of surface processes.

There are essentially three methods for experimental determination of the heat of adsorption: (1) calculation from adsorption equilibrium data; (2) calculation from desorption kinetics data; (3) calorimetric measurement.

In regards to the first method, since adsorption processes are exothermic, we shall adopt the usual convention, assigning the differential molar adsorption heat,  $q$ , as the negative of the differential molar enthalpy change for the process. Isothermic adsorption heats,  $q_{st}$ , are determined under equilibrium conditions using the Clausius-Clapeyron equation:

$$\Delta_{st}(\theta) = -R \left( \frac{P}{1-\theta} \right)_\theta \quad (1.1)$$

where  $R$  is the gas constant,  $P$  is the pressure,  $T$  is the temperature, and  $\theta$  is the fractional surface coverage. Usually, isosteres are usually obtained by determining the pressure and

temperature required to give a known coverage, and it is therefore important to monitor the coverage. To obtain the heat of adsorption, either isotherms or isobars are used, and once several have been obtained, a Clausius-Clapeyron plot is derived. However, the major disadvantage of this technique is that it can never be used to measure the heat of adsorption for an irreversible process.

The second method widely employed to estimate adsorption heats is through the measurement of the desorption energy,  $E_d$ . This method is more straightforward and is, hence, more commonly used. With a high pumping speed and a low heating rate ( ), the desorption rate can be shown to be proportional to the observed pressure increase,  $P$ . The Redhead equation for first-order desorption is then used to relate  $E_d$  to the temperature at which a desorption peak occurs<sup>[3]</sup>:

$$\frac{E_d}{kT} = \ln\left(\frac{A}{b}\right) - 3 \cdot \ln\left(\frac{P}{P_0}\right) \quad (1.2)$$

where  $A$  is the frequency factor for the desorption process. Formally, this only applies when  $E_d$  and  $A$  are independent of  $\theta$ . Hence, the desorption energy can be determined at various initial coverages. This method is simple but has several disadvantages. It requires a precise knowledge of the desorption rate law, and this must also include information about how all of the kinetic parameters vary with coverage. Another disadvantage is that some gases, such as oxygen, dissolve in the metal bulk when heated and it has therefore been impossible to obtain desorption spectra for them.

This, there is a tremendous need for direct calorimetric measurements of adsorption energies on single crystal surface. The most recent advances in calorimetry on surface was the development of the single-crystal adsorption calorimetry by David King's group, which provided the first opportunity to measure accurate, coverage-dependent adsorption heats on well-defined surface, where a direct correlation with structural and spectroscopic results could be made<sup>[4-6]</sup>. The calorimetric determination of heat of adsorption does not require any model of the surface process and measure the heat directly. The method thus works both reversible and irreversible processes. Metastable states, coadsorption and displacement can only be studied by calorimetry. Moreover, the calorimetric measurement occurs unlike the other two methods, at a fixed temperature. The development of the SCAC technique has opened up accurate heat measurement to many

different surface processes which have not been measured before. Very recently in 1997, a SCAC has been built by Campbell and co-workers specifically to measure metal vapor adsorption<sup>[7]</sup> and another is currently being developed by Dixon Warren et al<sup>[8]</sup>. These will help to further establish SCAC as one of the regular analytical tools used for investigating surface processes.

## 2. THE SINGLE-CRYSTAL ADSORPTION CALORIMETER

### 2.1 Thermodynamics

In SCAC, it is the energy released during the adsorption of a small increment of adsorbate at a fixed coverage, the *differential heat*,  $q_d$ , that is measured. The term differential heat of adsorption refers to the heat released in an incremental adsorption following a path I which no work is performed, i.e.,

$$d_q = \Omega_{g-a} = \Omega_g - \Omega_a \quad (2.1)$$

where  $U_g$  is the molar energy of the gas,  $\Omega_a$  is the differential or partial molar energy of the adsorbate. In the usual calorimetric experiment the adsorption surface area is constant and the substrate is assumed to be thermodynamically inert, so that the only work done is the gas-phase pressure-volume work, which may be shown as:

$$d_c = -P \frac{dn_a}{V_g} \quad (2.2)$$

Here,  $P$  and  $V_g$  are the gas-phase pressure and volume and  $n_a$  is the number of moles of adsorbate. Since  $q_c$  is the order of  $RT$ , the calorimetric heat,  $q_{cal}$ , measured in an experiment for a fully reversible process is:

$$q_{cal} = q_d + RT \quad (2.3)$$

We will define the “heat of adsorption” ( $q_{ad}$ ) at room temperature as the negative of the *standard enthalpy change* ( $\Delta H_{ad}$ ) for the same reaction. The heat of adsorption and standard enthalpy change upon adsorption at the sample temperature are then given by:

$$q_{ad} = -\Delta H_{ad} = q_d + RT \quad (2.4)$$

## 2.2 Experiment

The essence of a calorimetry experiment is shown in Fig.1 [4]. During an experiment, a pulsed molecular beam is directed at the front face of a single-crystal film. A proportion of these molecules adsorbs at the surface and causes the liberation of adsorption heat within the surface region. During the experiment, a single crystal, approximately 200nm thick and  $1\text{cm}^2$  in area, epitaxially grown on cut NaCl crystals and floated off in water, is mounted in an UHV apparatus (base pressure of  $5\times 10^{-11}$ mbar). Each crystal is supported on a ring made of the same material which has a 4-mm diam hole in the center. The surface was cleaned by argon ion sputtering and annealing cycles. Adsorption only occurred onto an  $\sim 2$ mm diameter circular spot in the center of the sample, which was thus unsupported over this area and had a very low heat capacity. The heat adsorption liberated in the film thus caused a measurable temperature rise up to 0.1K. The heat was considered to be mainly lost by radiation. The temperature of the crystal is measured remotely to avoid increasing its heat capacity. For this purpose, the back face of the crystal is coated thinly with amorphous carbon from a candle flame, giving it a high emissivity. Most of the radiation, therefore, occurs from the back face of the crystal, and this emitted infrared light is collected and focused onto a mercury cadmium telluride (MCT) detector which is mounted outside the experimental chamber.

The gas delivered onto the front face of the crystal in a supersonic molecular beam (see Fig. 2). To maximize the temperature rise at the same sample and to improve detectability of this rise it was desirable that adsorption should take place quickly and for

this reason the beam was pulsed. The pulse of a width of 50ms comprised approximately  $10^{12}$  molecules. The repetition rate of about 2s ensured that there was complete cooling between pulses. The beam is carefully collimated so as to minimize the penumbra and obtain a uniform intensity across the dosing area. The 2mm diameter beamed area of the crystal had a heat capacity of the order of  $10^{-6}\text{JK}^{-1}$ . A heat increment of  $10^{-8}\text{J}$  thus gave a measurable IR radiation signal. The temperature rise at the crystal for  $\sim 1\%$  monolayer increments amounted typically to tens of mK.

The amount of heat generated by an adsorption pulse is calibrated by pulsing a known amount of power into the sample using a chopped laser beam with spatial and temporal shape close to that of the molecular beam. The laser beam passes through a biconvex lens to give a slightly divergent beam which is then passed into the system, and a prism reflects it down the molecular beam axis. It is thus cropped by the same collimating apertures as the beam itself to give the same spot profile at the crystal. The infrared signal resulting from heating of the crystal by the He-Ne laser is collected and analyzed in the same way as the adsorption signal. The laser power is measured outside the KBr window using an absolutely calibrated photodiode.

Gas molecules that do not adsorb are scattered back into the gas phase, producing a partial-pressure rise in the experimental chamber. This is monitored with a mass spectrometer, and thus the relative adsorbed amount or sticking probability can be inferred. The King and Wells technique is used<sup>[9]</sup>, based on a comparison with the scattered flux from an inert (gold) surface. The beam intensity, typically of the order of  $\sim 10^{12}$  molecules per pulse, is calibrated absolutely with a spinning rotor gauge so that the amount adsorbed can be accurately determined at each stage and summed to give the accumulated coverage. The absolute energy is determined by laser calibration and, with the amount adsorbed, this yields an absolute molar adsorption heat for each pulse of gas. Furthermore, an absolute coverage scale is obtained against which the adsorption heat and the sticking probability can be plotted. However, when the heat of adsorption falls, desorption becomes appreciable between pulses, and finally a steady state is attained whereby the amount of gas added during each pulse is balanced exactly by the quantity of gas that desorbs between pulses. Summing the sticking contributions given by the finite

sticking probability measured for each pulse thus yields an apparent coverage scale that extends indefinitely: the true coverage must reach some definite limit.

### 3. CALORIMETRIC MEASUREMENTS

#### 3.1 CO adsorption on Pt(111)

The adsorption of CO on Pt surface has been extensively studied due to its industrial importance in various catalytic processes, such as Fischer-Tropsch synthesis and CO oxidation in car exhaust catalytic converters.

The microcalorimetric results for CO adsorption on Pt(111), averaged over six experimental runs, are shown in Fig. 3<sup>[5]</sup>. The heat of adsorption of CO at 300 K is initially 183 ± 8 kJ/mol, declining to about 118 kJ/mol at the expected saturation coverage of 0.50 ML. Meanwhile, from the figure, we could find that the gradient of the heat curve changes at about 0.36 ML coverage. Former LEED experiments<sup>[10]</sup> show a (3 × 3)R30° ordered layer would obtain at θ = 0.33 ML, and a c(4 × 2) structure at around 0.50 ML. The steady-state heat achieved at the saturation coverage of 0.5 ML was 60 ± 4 kJ/mol.

From the coverage-dependent heats of adsorption, a simple analysis to extract the adsorbate interaction is possible. At θ = 0.33 ML a (3 × 3)R30° ordered layer forms and this corresponds to a heat of 160 kJ/mol. The observed structure is shown in Fig. 4a. At this coverage, each CO adsorbate will be surrounded by six next nearest neighbors (6nnn), so the nnn interactions  $\epsilon_2$  can be estimated as

$$\epsilon_2 = \frac{q_0 - q_{0.33}}{6} = 3.8 \text{ kJ/mol}$$

where  $q_0$  is the initial differential heat of adsorption and  $q_{0.33}$  is the heat of adsorption at 0.33 ML coverage.

The same calculation can be performed at θ = 0.5 ML coverage where a c(4 × 2) structure is observed (Fig. 4b). Each adsorbate is now surrounded by four CO molecules on bridge sites and four CO on atop sites. Thus, the differential heat at this coverage is,

$$q_{0.5} = 0.2q_0(\text{on-top}) - \epsilon_{\text{on-top}} - \epsilon_{\text{bridge}} + 0.2q_0(\text{bridge}) - \epsilon_{\text{on-top}} - \epsilon_{\text{bridge}}$$

where  $q_0$  (on-top) is the heat of adsorption on the top sites (equivalent to the initial heat of adsorption)  $q_0$  (bridge) is the heat of adsorption on the bridge sites, and  $\epsilon_b$  is the

interaction energy between an adsorbate on an atop site and one on a bridge site. We then have the expression:

$$d_0(\text{Pt}(110)) - 80\text{p} = 83 \cdot \text{TK} \setminus \text{MOI}$$

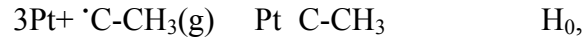
Meanwhile, extensive information has been gained on the mechanism of oxygen chemisorption and oxide formation on the low-index single crystal planes of nickel and on the role of the potassium precoverage in the bonding of adspecies. Similar studies were carried out with the chemisorption of CO and nitrous oxide NO on different surfaces<sup>[11-13]</sup>.

### 3.1 Reaction with surface products: the adsorption of hydrocarbons

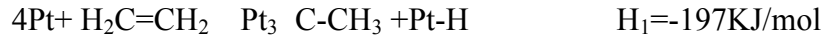
The adsorption of hydrocarbons is a complex, with surface reactions often occurring upon adsorption at 300K. Hydrocarbon reactions are a fundamental part of many catalytic processes, and an understanding of the energetics of adsorption is essential. Due to the irreversible nature of the process, no adsorption heats had been measured for hydrocarbons before 1998. Some of the different species can be formed upon adsorption of ethylene or acetylene onto a surface.

Fig. 5 shows the measurement of the heat of adsorption for C<sub>2</sub>H<sub>4</sub> on the Pt(110)-(1×2) surface at 300K<sup>[14-15]</sup>. The initial heat is 235KJ/mol, and there are then several distinct regimes before a steady-state heat of 140KJ/mol is reached. The different heat adsorption are the results of different species observed on the surface. By comparison with other authors, it is suggested that the first species formed on the Pt(110) surface is ( C-CH<sub>2</sub>-), which bonds to the surface in the throughs of the (1×2) missing-row reconstruction. The next species to be formed on the surface is ( C-CH<sub>3</sub>), probably on the (111) microfacets of the Pt(110) reconstructed surface. Above 0.5ML coverage, di- -bonded ethylene and then -bonded ethylene are found on the surface. The heats of reaction for the different species on the surface can be used to obtain average values for the C-Pt bond energies.

An example of how these values are calculated using the above method is illustrated for ethylidyne. The C-Pt bond formation reaction is



and the enthalpy for this reaction can be obtained from the reaction heats of the following processes:



The value of  $H_1$  can be obtained from the measurement of SCAC experiment;  $H_2$  is the heat of adsorption of  $\text{H}_2$  on Pt(110), and  $H_3$  was calculated from the average bond energies of the C=C, C-C, and C-H bonds. Combining these would get  $H_0 = -716 \text{KJ/mol}$ . Therefore, the C-Pt single bond energy for ethylidyne on Pt(110) is estimated as 239KJ/mol.

#### 4. NEW DEVELOPMENT

Several improvements are being made to the system that will produce a higher signal, increase the accuracy, and reduce the noise level. To make measurements with the crystal at low temperatures feasible (the radiation power at small temperature difference  $T$  is from the Stefan-Boltzmann law proportional to  $T^3$  and thus it rapidly decreases with falling temperature), and to remove uncertainties in the crystal temperature arising from the proximity of the cooled IR radiation detector, the pyroelectric sensing of the single crystal temperature was adapted<sup>[2]</sup>. In this work, all other aspects of the calorimeter were identical with that based on infrared remote sensing. A pyroelectric  $\text{LiTaO}_3$  wafer 0.3mm thick was used, coated on both sides with AuCr electrodes. The thin-film crystal is cold-welded onto the pyroelectric material. The detector consists of a  $\text{LiTaO}_3$  wafer clamped onto a special mount which is attached to the end of the sample manipulator in the UHV chamber. A schematic diagram is shown in Fig.6. The range of the measurements was thus extended down to 90K, while the upper limit reached 410K. The measured temperature rise due to a single pulse of gas was as low as  $2.5 \times 10^{-5}$  K. The heats of adsorption of oxygen obtained at 300K on different Ni(100) samples using the pyroelectric detector and the infrared emission showed a very good overall agreement

except for low coverages where the former method gave approximately 15% lower values. However, there were problems with microphonic noise in the pyroelectric experiments, and a compensating detector system should be used to reduce the sensitivity to this noise. Meanwhile, this system does require ca.1 h to reach a stable temperature, and it is difficult to avoid background contamination over this time scale. The remote sensing detector system does not suffer from this problem. Improvement of the pyroelectric calorimeter aimed at increasing its thermal stability and signal-to-noise ratio were announced to be underway.

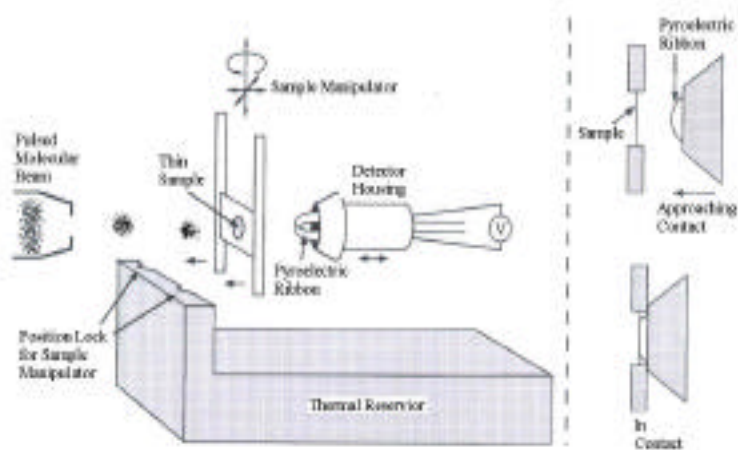


Fig. 4. Schematic diagram of Campbell's calorimeter showing the pyroelectric detector. The right side shows an expanded side view of the detector approaching contact (top) and in contact (bottom) with the sample<sup>[16]</sup>.

In 1997, a new microcalorimeter is described by C. T. Campbell<sup>[16]</sup>. The principle is similar to that of the Cambridge calorimeter, a schematic diagram of the system is shown in Fig.7. Their novel heat detector is a 9mm thick pyroelectric polymer ribbon, which is mechanically driven to make a gentle mechanical/thermal contact to the back of the single-crystal sample during measurements. The detector can be removed from the sample to allow high-temperature sample preparation to take place, which is not possible with the Cambridge system. Other advantages include use of thicker samples (1 $\mu$ m), and potential measurements at cryogenic temperatures. Meanwhile, a novel chopped molecular beam of metal vapor and a method of correcting for absorbed radiation from the hot effusion cell are also described. Recently, they reported the heat of adsorption of

Pb on an MgO(100) thin film at 190K measured calorimetrically as a function of coverage using this removable pyroelectric polymer ribbon as the heat-detecting element<sup>[17]</sup>. This is the first demonstration that this versatile method of heat detection can be used for single-crystal adsorption calorimetry at cryogenic conditions. Meanwhile, from the experiment, metal/substrate adhesion energies can also be extracted. They could obtain pulse-to-pulse standard deviations of <2% in the heat of adsorption for pulses containing <0.03 ML of Pb, and absolute accuracy to within a few percent.

A number of significant refinements were further made in the molecular beam system, flux calibration system (e.g. a spinning rotor gauge was used to determine the pressure) and sticking probability measurement technique. The sensitivity and accuracy of the calorimeter have thus been considerably raised. The precision of the measurements was limited mainly by the uncertainty in the sticking measurement rather than by uncertainty in the heat measurement. Some further uncertainty might be due to the molecular beam flux measurement, the laser calibration of the sample heat capacity and emissivity, and finally to the possible occurrence of residual surface contamination or disorder below the Auger and LEED detection limits.

## 5. CONCLUSION

The newly developed single-crystal adsorption calorimetry is particularly important to the understanding of surface reactivity and catalysis at metal surfaces. Its advantages include:

1. The most important advantage of calorimetry is that irreversible adsorption processes can be studied, where adsorption, reaction heats, and bond energies have not been previously measured for single crystal surface.
2. From the adsorption heats at high coverage when a steady-state regime was established, the entropy change of adsorption, the differential entropy of adsorbed species and the frequency factor for desorption were calculated.
3. Apart from providing heat data, adsorption calorimetry has contributed to the growing understanding of surface process due to the effort at an interpretation of the measured results, mostly in combination with other methods. For example, on Pt, the highest

heat as observed on the metastable (100)-(1×1) surface; the lower value for the initially hex surface is accounted for by the additional energy required to reconstruct this surface to (1×1) during the adsorption process.

4. Perhaps the most important message from the calorimetric studies to date is the magnitude of atom-atom interaction energies, which have been determined from the coverage dependence of the calorimetric heats.
5. Modifications to the original design mean that the SCAC is capable of measuring molar adsorption heats for systems with a high sticking probability down to a detection limit of  $\sim 10 \text{ kJ mol}^{-1}$ , with an estimated absolute accuracy of 6% or even better<sup>[16]</sup> for adsorption heats greater than  $\sim 80 \text{ kJ mol}^{-1}$ . By means of averaging the data from several runs, accurate heats could be measured for system with sticking probabilities as low as 0.03. The range of the measurements was thus extended down to 90K, while the upper limit reached 410K.

The measurements on single crystal planes have thus started a new era in adsorption calorimetry and have ranked this method among the tools of the surface science of today. Further perfection of the instrument is underway.

However, no studies have been carried out on many important semiconductor and oxide surfaces which remains a challenge for further instrumental development work.

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