

## Adsorption calorimetry on filaments, vacuum-evaporated films and single crystals of metals

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### Abstract

A review is given of calorimetric methods for the determination of the heat of adsorption of gases on surfaces at least partially defined for their crystal structure and cleanliness, i.e. on filaments, vacuum-evaporated films and single crystals of metals. The main features of the particular methods are mentioned, and the contribution of the obtained results to the development of insight into the physics and chemistry of surface processes is outlined. © 1998 Elsevier Science B.V.

*Keywords:* Adsorption calorimetry; Filaments; Vacuum-evaporated films

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### 1. Introduction

Heat of adsorption of a gas on a solid is, in general, composed of several contributions, including energy of the formed surface bond, energy associated with perturbation (or even dissociation) of the adsorbate, energy of interactions between the adparticles and energy associated with the surface relaxation or rearrangement. In the basic research of adsorption it is frequently desirable to separate the individual terms. In order to facilitate such a separation, and to minimize the complicating effects of the polycrystallinity and contamination of the surface, it is desirable to carry out the experiments with surfaces which are at least partially defined for their crystal structure and cleanliness. Such surfaces can be obtained with metal filaments, vacuum-evaporated thin films, and single crystals of metals.

The first calorimetric experiments with this class of surfaces date back to the 1930s, when Roberts [4,5] designed a calorimeter for the determination of the heat of adsorption of gases on annealed, fine wires of metals. In the 1940s, adsorption calorimetry on vacuum-evaporated metal films was advanced. In the following decades, this method was considerably developed and widely used as a source of energetic data needed to increase the theoretical understanding of chemisorption and catalysis on metals. In the beginning of the 1990s, a calorimeter for the measurement of heats of adsorption on single-crystal planes of metals was designed and put into operation. This started a new area in adsorption calorimetry on well-defined surfaces, and the method has thus ranked among the specialized powerful tools for contemporary surface science studies.

The particular methods and the most important results of their applications are briefly outlined in the following text. More detailed information, including a complete list of the studied systems and of the obtained heats is given in a review article [1].

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## 2. Adsorption calorimetry on metal filaments

### 2.1. Method

Around 1930, Roberts was one of those who recognized that the adsorption behavior of a clean surface may be quite different from that of a surface with preadsorbed particles and, therefore, pioneered adsorption studies on clean surfaces of metals. In this context, Roberts worked out a calorimetric method yielding heat of chemisorption of gases on a tungsten filament whose surface was cleaned by flashing over 2300 K [2,3]. The filament was then rapidly cooled in vacuum to room temperature at which temperature the adsorption of a gas dose was completed in the few moments before contamination could occur. The filament (28 cm long, 0.0066 cm in diameter, surface area 0.58 cm<sup>2</sup>) served both, as adsorbent and as its own resistance thermometer. It constituted one arm of a Wheatstone bridge, by means of which its temperature changes due to the released heat of chemisorption were determined. The total temperature change of the order of 10<sup>-2</sup> K, corresponding to a gas dose of the order of 10<sup>-14</sup> molecules, was converted into the heat value using the heat capacity of the filament as

calculated from its mass and specific heat. Its cleanliness after flashing was checked by determining the accommodation coefficient of neon which was found markedly dependent on the extent of contamination.

By repeating the procedure for the incrementally dosed gas, differential heat as a function of the coverage was obtained. The surface coverage could be estimated when it was assumed that the exposed crystal planes, their relative number, and the roughness factor of the surface are known, and that each surface atom can bind one adparticle. In the following decades, the original Roberts device was significantly improved so as to furnish high quality data (Fig. 1) [4].

The advantage of the method is that the filaments can be used repeatedly after cleaning them by flashing. The structure and cleanliness of the surface can thus be well reproduced from one experiment to another. The duration of a run is in seconds. On the other hand, the method has major limitations. First, it is confined to filaments of metals which can be flashed to high temperatures without losing stability of the resistance and changing crystallographic structure of the surface. Second, the method is appropriate for rapid processes only where heat exchange by conduction through

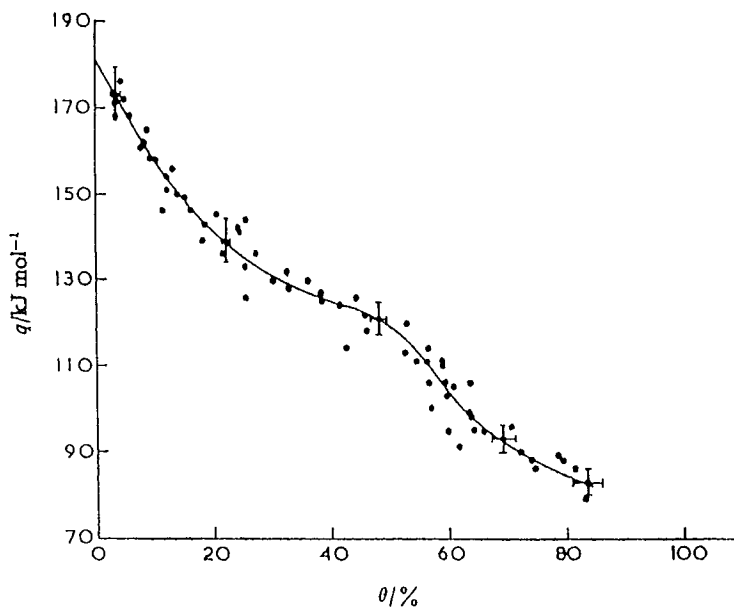


Fig. 1. The heat of adsorption of hydrogen on a tungsten filament at 287 K as measured by Couper and John [4] in a Roberts-type calorimeter.

unadsorbed gas is negligible and both, the total temperature change and the amount of adsorbed gas can be determined. Third, estimation of the surface coverage involves the above-mentioned uncertain assumptions concerning the structure of the surface and occupation of sites. Fourth, use of very thin filaments with a view to increasing sensitivity of the calorimeter, may cause demetallization of the surface atoms (withdrawal of a sizable portion of electrons from conduction process by their involvement in the chemisorption bond) which simulates temperature-induced increase of the resistance. Finally, building and operation of the calorimeter requires considerable skill and experience.

## 2.2. Results

The Roberts method has been applied to a few adsorption system only, including W/H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>; Ni/H<sub>2</sub>; Pd/H<sub>2</sub>; Pt/H<sub>2</sub>; Ta/N<sub>2</sub> [1], at temperatures in the 77–382 K range (in one case, even up to 950 K). The calorimetric measurements were mostly combined with the determination of sticking probability and flash desorption spectra.

The objects of the experiments were several:

- (i) to identify the nature of adsorption sites and of the corresponding states of the adparticles;
- (ii) to assess the relative importance of the a priori heterogeneity and the induced heterogeneity, and to estimate the interaction energy between the adparticles;
- (iii) to discern mobility or immobility of the adparticles;
- (iv) to reveal the existence of precursors and to estimate their mobility.

The high initial heat in all systems was indicative of dissociative chemisorption on the bare surface. However, an interpretation of the coverage dependence of the heat was not so unambiguous, since an experimental heat–coverage curve can be fitted by different adsorption models. For example, the effect of site-energy distribution on a heterogeneous surface can be the same for mobile adsorption as the effect of repulsive interactions between immobile adparticles on a homogeneous surface. The situation can be still more complex if the final chemisorbed state is reached through a more weakly bound precursor that may

be mobile or immobile. By selecting appropriate values of the relevant parameters, one thus has a wide field for speculation about the operating adsorption model. The ambiguity can be only partially reduced by taking into account results of other methods, such as sticking probabilities and desorption spectra.

In this way, although the adsorption heats measured with filaments played an important role in the build-up of knowledge of surface processes, it became gradually clear that it is essential to have data measured on surfaces exposing a single, well-defined crystal plane for further progress. Since such measurements were not accomplished with filaments, this calorimetric technique has not been pursued since the 1970s.

## 3. Adsorption calorimetry on vacuum-evaporated films

### 3.1. The method

Thin films of metals, prepared by condensation of metal atoms onto a glass support after their evaporation in vacuo from a wire or fragment, were introduced into the research of adsorption and catalysis on the gas–solid interface in the mid-1930s [5–7]. The surface area of films was orders of magnitude higher than that of wires, whereby the experiments were enormously facilitated; and their surface could be prepared and maintained in a much cleaner state than that of granules, powders and foils which never can be completely rid of firmly chemisorbed oxygen species, etc. The widespread application of vacuum-evaporated films in the research of surface phenomena was stimulated by Beeck et al. [8,9], who systematically employed films of transition metals for the investigation of catalytic processes. They endeavoured to elucidate reaction mechanism on the basis of the heat of adsorption of the reactants [8], and to this end they designed an adsorption calorimeter for work with films [9].

The Beeck calorimeter was suitable for the determination of small amounts of heat produced in a few tens of seconds at the most, at room and liquid-air temperatures. It consisted of a thin-walled glass ampoule of 15–20 mm diameter, mounted in an evacuable jacket immersed in a thermostatic bath. In the axis of the ampoule was hung a hair-pin shaped wire

from which the film was evaporated onto the inside of the evacuated ampoule. Onto its outer wall was wound a platinum wire, serving as a resistance thermometer. Calibration of the calorimeter was effected in Beeck's original experiments by calculating its heat capacity from the weight and specific heat of the components. The heat capacity was a few joules per Kelvin. The gas was dosed to the film from an attached volumetric adsorption apparatus.

The Beeck calorimeter was considerably improved [1] in the following decades. Its sensitivity was increased so that a typical gas dosed was of the order of  $10^{-8}$  mol and the released heat of  $10^{-3}$  J brought about a temperature change of  $\approx 10^{-3}$  K; the electrical circuit was substantially modernized; the background pressure during and after the film deposition was of  $10^{-9}$ – $10^{-10}$  mbar; the calibration was carried out by means of electrical heat (Fig. 2). Also, the processing of the measured data was significantly refined.

Later on, Wedler [10,11] designed a spherical calorimeter (Fig. 3) to facilitate uniform distribution of the admitted gas and to make feasible the determination of the electrical resistivity of the film simultaneously with the measurement of adsorption heat. In this way, the kinetics of the heat generation were obtained. The thin-walled bulb was  $\approx 5$  cm in diameter, and thin platinum foils, sealed to the inner wall of the bulb, served both for delivering the calibration current to the film and for the measurement of the film resistivity. Experiments in film calorimeters were carried out mostly at room temperature, rarely at 77 K, and exceptionally at elevated temperature between 323 and 373 K [1].

A principal limitation of film calorimeters is that they can be applied to rapid adsorption processes only, in which the equilibrium gas pressure above the film, after a dose admission, soon drops to  $10^{-4}$ – $10^{-5}$  mbar and less. In such a case, the heat released in the calorimeter, at room temperature, is dissipated to the thermostat virtually entirely by radiation across the evacuated jacket [12]. At low temperatures, when the heat transport by radiation becomes less effective, the jacket is filled with a gas up to  $10^{-2}$ – $10^{-3}$  mbar, in order to ensure that the heat is lost from the calorimeter to the thermostat predominantly by conduction through this gas. In both cases, the rate of the heat dissipation is described by Newton's law of cooling

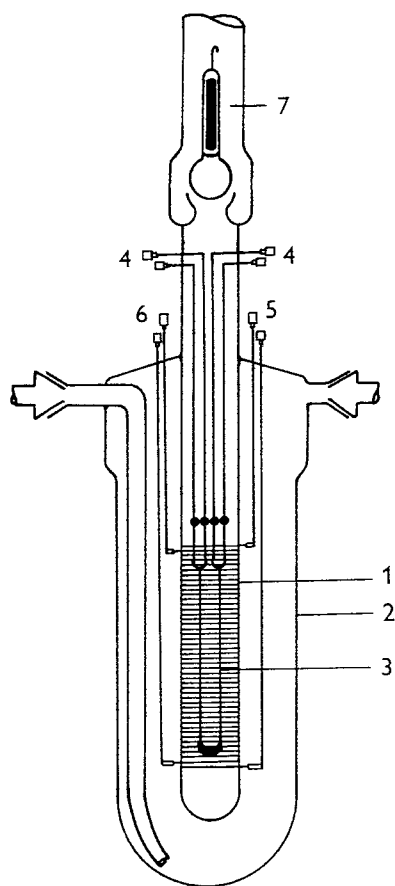


Fig. 2. Cylindrical film calorimeter (version designed in the author's laboratory). 1 – Thin-walled glass ampoule with coiled resistance thermometer and calibration heater; 2 – jacket; 3 – evaporation wire; 4 – terminals of the evaporation wire; 5,6 – terminals of the resistance thermometer and the calibration heater, respectively; and 7 – magnetically operated ground-ball valve.

with a single rate constant (the Stefan–Boltzmann radiation law approximates the Newton's law for small temperature differences between the radiating body and the surroundings [1,12]). If, however, the adsorption is slow, an appreciable portion of the heat is lost to the surroundings by conduction through the unadsorbed gas whose pressure gradually decreases. As a result, the over-all rate of the heat dissipation changes, the simple Newton's law of cooling does not apply, and the ordinary evaluation of the evolved heat on the basis of the Tian equation is not practicable [1,12]. In addition, the simple construction and high sensitivity of the calorimeter cannot prevent the dis-

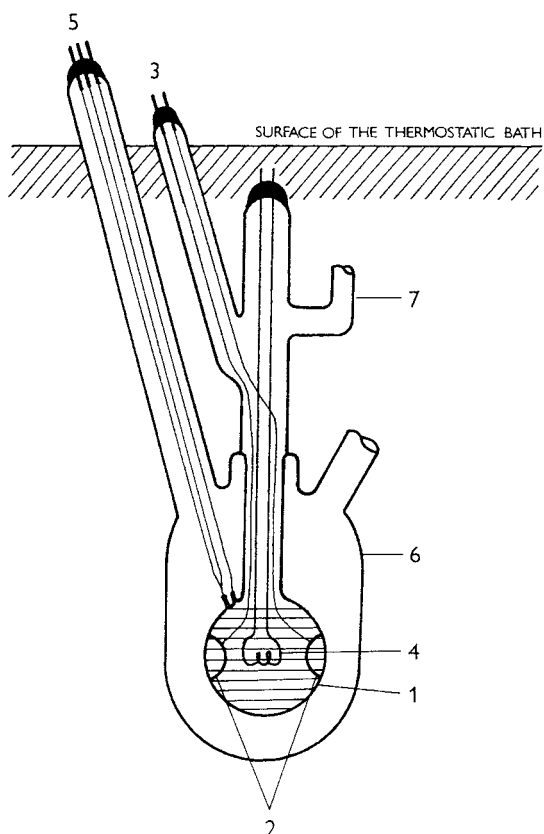


Fig. 3. Spherical film calorimeter as designed by Wedler et al. [11]. 1 – Thin-walled glass cell with coiled resistance thermometer; 2 – platinum contact foils used for input of the calibration heat to the film and for measurement of the film resistivity; 3 – terminals of the contact foils; 4 – evaporation wire; 5 – terminals of the resistance thermometer; 6 – jacket; and 7 – connection to the adsorption apparatus.

turbing effect of fluctuations in the ambient temperature when the time scale of the experiment is long. In practice, the time constant of film calorimeters is ca. 100 s, and production of the essential portion of the heat should not exceed ca. 15–20 s.

### 3.2. Results

While adsorption calorimetry on filaments was primarily concerned with the physical state and properties of the adspecies, the ultimate goal strived for by Beeck et al. in the measurements with metal films was to reveal the influence of the electronic and geometric structure of the particular metals on their behavior in

catalytic reactions. The above authors established a correlation [8] between the initial heats of adsorption of ethylene and hydrogen, i.e. the heats of the bare surface (which were regarded as a measure of the strength of the formed surface bonds), the percent *d*-character of the metal (introduced in Pauling's theory of the chemical bond as a measure of the distribution of *d*-electrons between the metal–metal bond and the surface bond [13]), the rate of hydrogenation of ethylene, and the interatomic distances in the crystal lattice. It was on this basis that the mechanism of the said hydrogenation reaction was suggested. Comparison of the heat of adsorption with catalytic activity of unoriented and oriented films (the latter films expose predominantly only one or a few low-index planes), led to estimates of the relative importance of the electronic and geometric structure in the particular processes on various metals.

Subsequently, however, the connection between the initial heat of adsorption and the catalytic behavior turned out not to be straightforward, since the initial heat concerns the most firmly bound adparticles, while adparticles, which are bound relatively weakly, are catalytically active. Considerations on the relationship between adsorption heat and catalysis can be found in the literature [14–17].

Early attempts to explain the mechanism of a catalytic reaction by specifying the formed surface species using the heats of adsorption and/or coadsorption at higher coverages concerned systems of selected transition metal films with pairs of simple gases ( $\text{H}_2 + \text{NH}_3$  [18],  $\text{H}_2 + \text{CO}$  [19]). Later on, numerous calorimetric studies with coadsorption of simple gases were reported (e.g. Refs. [11,20–22]). However, the obtained pieces of information on the displacement of preadsorbed species, blocking of sites, and/or on the formation of surface complexes were of limited value for catalytic research.

The main importance of calorimetry on metal films has been in providing heats of chemisorption as a function of adsorbed amount and in some cases, of temperature, for a large series of gas–metal systems. These heats represented for decades the most reliable experimental values on the energetics of chemisorption (in particular, of the energy of the formed surface bond), and were used in numerous correlations concerning surface phenomena, as well as for verification of the results of theoretical calculations. Only recently,

their importance began to decline due to the advent of adsorption calorimetry on single crystal planes (see Section 6).

Among the most extensively studied problems belongs the interaction of oxygen with films of transition metals. The initial heat, in conjunction with the coverage dependence of the heat, was used [23] to distinguish oxygen chemisorption from oxidation; to propose the mechanism of growth of the adsorbed layer and of the oxide layer; to delineate the configuration of adparticles on particular crystal planes to reveal the probable precursor species; etc. Similarly, the heat-coverage curves of carbon monoxide on a variety of transition metals [24] yielded the extent of CO dissociation which diminished with increasing adsorbed amount; the strength of the adsorbate bonding to the surface; the ratio of the linear and bridge form of CO admolecule; the number of bonds in which one surface atom can participate; the interaction energy between the adspecies; etc. Results of further studies of CO behavior on Fe and Ni are also available (e.g. in Ref. [11] and references therein).

The heats of chemisorption for a series of low-weight saturated and unsaturated hydrocarbons on metals of different chemisorption and catalytic activity [25–29] permitted determination of the reactivity of bonds in the given hydrocarbon molecules as well as models of the structure of the adspecies formed at low surface coverage. It also yielded estimates of the energy of the carbon-to-metal bonds.

Comparison of the heats measured at room and low temperatures was informative. The extent of CO<sub>2</sub> dissociation was found to diminish with decreasing temperature and increasing coverage [24] and an intermediate state which was not observed at 195 K was likely formed at 273 K at low coverage [30]. The temperature-dependent states of adsorbed oxygen were revealed on some metals [31]. Hydrogen adspecies were shown to occur in different adsorption states with decreasing surface mobility when the temperature was lowered [32]. The heats measured for hydrogen on films of iron at room and elevated temperatures pointed to an adsorption-induced reconstruction of the film surface [33].

Further, some information on the rate of heat evolution could be deduced from the shape of the recorded temperature–time trace. Qualitatively, protracted

release of heat signalled occurrence of an activation energy for the adsorption process [25–29]. In spherical calorimeters of the Wedler type, where heat production and the change in the electrical resistivity of the film were monitored simultaneously, an explicit analytical expression for the kinetics of the heat process was obtained [34]. By comparing the cooling part of the temperature–time trace observed in electrical calibration, and in an adsorption run, it was possible to detect an exothermic or endothermic process taking place in the adlayer. For a consecutive process of the first order, the kinetic as well as the energetic parameters were derived, describing the formation of the intermediate and final adsorption states. A deconvolution programme enabled the true kinetics of heat generation cleared of thermal lags to be extracted from the recorded temperature–time trace in a cylindrical calorimeter [35].

Experiments in film calorimeters were frequently complemented by temperature-programmed desorption, measurement of changes in work function and electrical resistance, X-ray photoelectron spectroscopy, and isotope exchange. A complete list of published experiments and results is given in a recent review article [1].

### 3.3. Summary

Adsorption calorimetry on vacuum-evaporated films has played an important role in the development of our understanding of chemisorption in the last half-century.

On the other hand, the results measured for the same gas–metal system, by different authors, frequently show considerable disagreement [1]. This is due to the fact that films are essentially polycrystalline, and are always contaminated to some degree by adsorption of residual gases and/or by diffusion of impurities from the bulk of the film. In-situ control of their structure and cleanliness is not feasible. Chemisorption is, however, sensitive to both, the structural details of the surface as well as the degree and nature of its contamination.

Further, Beeck-type calorimeters are not suitable for measurement of slowly released heat due to reasons mentioned in the above outline of the method.

Efforts at overcoming these drawbacks led to the novel approaches described in the following.

#### 4. Adsorption calorimetry on single-crystal discs

The first serious attempt at overcoming the negative implications of the calorimetric measurement of heat of adsorption on polycrystalline samples (see Section 6) was published in 1986 [36]. The authors used as adsorbent a polished single-crystal disc of Pt(111), about 10 mm in diameter. Two miniature thermistors were fitted into holes drilled in the side of the disc. One thermistor functioned as a temperature sensor, the other as a source of calibration heat. Typically, a dose of  $10^{-9}$  mol CO produced a temperature rise of  $10^{-4}$ – $10^{-3}$  K. The disc was mounted in an UHV apparatus with a background pressure of the order of  $10^{-11}$  mbar, and it was cleaned before the experiment by heating in oxygen at  $\sim 900$  K and flashing to  $\sim 1500$  K using electron bombardment, until no impurities could be detected by in-situ Auger electron spectroscopy.

The principal problem was the high thermal capacity of the disc, namely its cooling to ambient temperature after the mentioned cleaning procedure took 10 to 12 h. During this period, ca. 30–50% of the surface was contaminated by adsorption of residual CO despite the very low background pressure in the apparatus. The heat of adsorption could, thus, be determined at high surface coverage only. In addition, the high-temperature induced uncontrolled changes in the structure of the single-crystal surface and in the sensitivity of the thermistor thermometer. Therefore, this method has not been further pursued.

#### 5. Pyroelectric calorimeter for polycrystalline metal samples

An effort at overcoming the applicability of the Beeck method to only rapid heat processes, was the driving force for the development of a novel technique, entirely different from the classic approaches. The main idea was to avoid the uncontrolled conduction of a part of the adsorption heat from the calorimeter via the unadsorbed gas above the film, by using a pyroelectric detector to monitor the temperature changes of the adsorbing surface onto which the adsorbate was dosed in a pulsed molecular beam [37–39].

Pyroelectric materials [40] have a permanent temperature-dependent electrical dipole along a particular crystalline axis. At a constant temperature, the internal charge distribution is neutralized by charges from the surroundings and from the bulk material; thus, no voltage is detectable at electrodes attached to the opposite surfaces of the pyroelectric crystal. Fluctuations in temperature induce fluctuations in polarization which, prior to their compensation by the mentioned changes, can be measured as voltage or current using a suitable circuit. A pyroelectric sensor thus reacts to a change in temperature rather than to its level, and the adsorbate should be therefore dosed to the adsorbing surface in pulses, which bring about pulses in the evolved heat. The molecules in a pulse, which after impinging onto the adsorbent are not adsorbed but reflected, are immediately pumped away and cannot thus be engaged in the conduction of the released heat from the calorimeter, as opposed to the classical film calorimeter of the Beeck type.

In addition, pyroelectric sensors are highly sensitive over a wide temperature range, they operate at room temperature without any cooling, and they allow the adsorbent sample to be miniaturized.

The outlined approach was realized in a prototype calorimetric device (see Fig. 4) [37–39]. A molecular beam was generated in a quasi-effusion source and mechanically chopped into pulses. These were sequentially collimated by a system of capillaries located in a differentially pumped chambers, and finally impinged on the adsorbent situated in the last chamber pumped down to a background pressure of the order of  $10^{-10}$  mbar. The collimating system was manufactured from quartz to prevent its deformation on heating in the degassing procedure. The other parts of the apparatus were made from glass.

A crystal of  $\text{LiTaO}_3$  was used as a pyroelectric sensor owing to its suitable electric and thermal parameters [40] and, most importantly, due to its high Curie temperature of 893 K, which allowed the apparatus to be baked out during outgassing. A polished wafer of  $\text{LiTaO}_3$  crystal of  $8 \times 8 \times 0.08$  mm size was placed in a manipulator which enabled the wafer to be rotated into the positions needed at the particular stages of the experiment. The wafer was coated on both sides with electrodes formed by thin layers of gold evaporated from a wire. The electrodes were switched into a circuit. Onto one electrode a film of

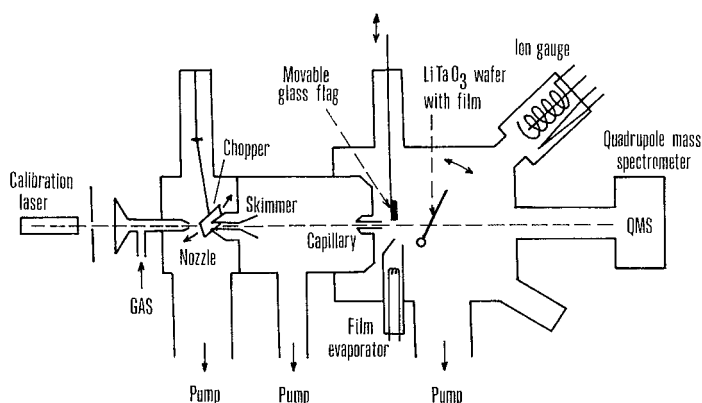


Fig. 4. Adsorption calorimeter for the measurement with vacuum-evaporated films using a pyroelectric temperature sensor and pulsed molecular beam [37–39].

the metal under study was evaporated in vacuum. This film was exposed to a pulsed beam of adsorbate molecules. The beamed area was ca.  $0.04 \text{ cm}^2$ , each pulse comprised  $\approx 10^{12}$  molecules and its width was between 0.5 and 1 s. Repetition period of ca. 2 s was sufficient to allow the calorimeter to cool down in the meantime.

Response of the  $\text{LiTaO}_3$  sensor in test experiments with adsorption of oxygen and carbon monoxide on films of dysprosium (the heat of adsorption in this system as measured in earlier Beeck-type calorimeter is very high) was very satisfactory (Fig. 5). The area of the peaks of current in a circuit connecting the gold electrodes should be proportional to the liberated heat. This was confirmed in calibration of the calorimeter by pulsed radiation of a HeNe laser which closely simulated the molecular beam in an adsorption run. The area of the peaks of current was exactly proportional to the delivered energy over a wide range.

In order to obtain molar heat of adsorption in the individual pulses and to assess the degree of surface coverage, it is necessary to determine the number of molecules adsorbed in a pulse. This is carried out by multiplying the number of molecules striking the film surface per pulse (calculated from the beam intensity measured using an ion gauge or quadrupole mass spectrometer) by the proportion of each pulse that was adsorbed, i.e. the sticking coefficient (it was determined by the King and Wells reflection-detector method [41]). In the given set-up, reproducibility of calibration of the gas-flux (molecular beam intensity) was not satisfactory. This, however, could be cleared

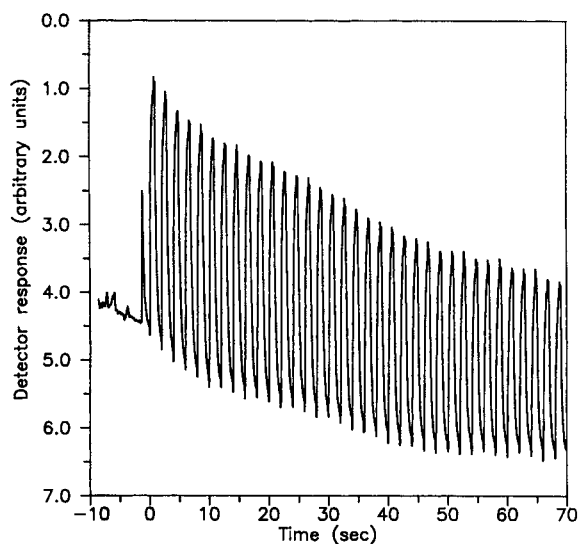


Fig. 5. Response of  $\text{LiTaO}_3$  sensor (pulses of current) to pulses of oxygen impinging on a film of dysprosium. The beam intensity was  $3 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$ , the width of a pulse and the repetition period were 0.93 s and 2 s, respectively. The beamed area was  $\approx 4 \text{ mm}^2$ .

away by a technical improvement of the apparatus, just like the disturbing effect of stray adsorption which would be prevented by a more efficient pumping to minimize re-adsorption of the molecules scattered from the beamed area of the film, on the unbeamed surface.

The novel method, thus, appeared to be basically sound and viable. In the meantime, however, an adsorption calorimeter allowing measurement on



single-crystal surfaces was designed and put into operation, as described in Section 6.

## 6. Adsorption calorimetry on single-crystal films

Independent of the development of the above-mentioned pyroelectric calorimeter, a sophisticated adsorption calorimeter using a pulsed molecular beam for gas dosing and an infrared radiation sensor of temperature was built and routinely employed for measurement on single-crystal surfaces of metals [42].

### 6.1. The method

The single-crystal calorimetric apparatus (Fig. 6) comprised an ultrahigh vacuum system which was specially manufactured to the authors' specifications and yielded a base pressure of  $5 \times 10^{-11}$  mbar. The built-in Auger and LEED devices provided an in-situ characterization of the cleanliness and crystallinity of the sample surface, respectively. The sample was a free-standing single-crystal film,  $\approx 200$  nm thick and  $1 \text{ cm}^2$  in area. It was epitaxially grown on macro-crystalline substrates with a suitable lattice constant, such as sodium chloride, which was thereafter dissolved in water. The single-crystal film was fixed by edges, so that its central part was unsupported and, consequently, had a very low heat capacity of  $\sim 10^{-6} \text{ J K}^{-1}$ . The adsorbate was delivered onto the sample in a supersonic molecular beam. To maximize

the temperature rise at the sample and to improve detectability of this rise, the beam was chopped into pulses of a width of 50 ms and a repetition rate of ca. 2 s. Each pulse comprised  $\approx 10^{12}$  molecules. The beamed area of the sample was only 2 mm in diameter.

The evolved heat of adsorption was dissipated predominantly by radiation since heat conduction through the thin film towards its edges was inefficient. The back of the sample was covered by a thin, highly emissive carbon layer to make faster the loss of the infrared radiation which was focussed onto a photoconductive mercury cadmium telluride broad-band photon detector situated at a distance of a few millimeters. The adsorbed amount was calculated from the measured beam flux and sticking coefficient, as outlined in Section 5. When the heat of adsorption was sufficiently reduced at high surface coverage, the number of molecules adsorbed in a pulse and desorbed prior to the subsequent pulse were equal to each other, so that the heat in the steady-state regime at saturation coverage could be measured [43,44]. The corresponding very small sticking probability of ca. 0.03 was determined by averaging the data from several runs [45].

Calibration of the calorimeter was conducted by HeNe laser beam pulsing in a way similar to that mentioned in Section 5.

It is important to note that the calorimeter can only measure the heat released during the time of detection of the infrared emission in a pulse, i.e. 50 ms. This

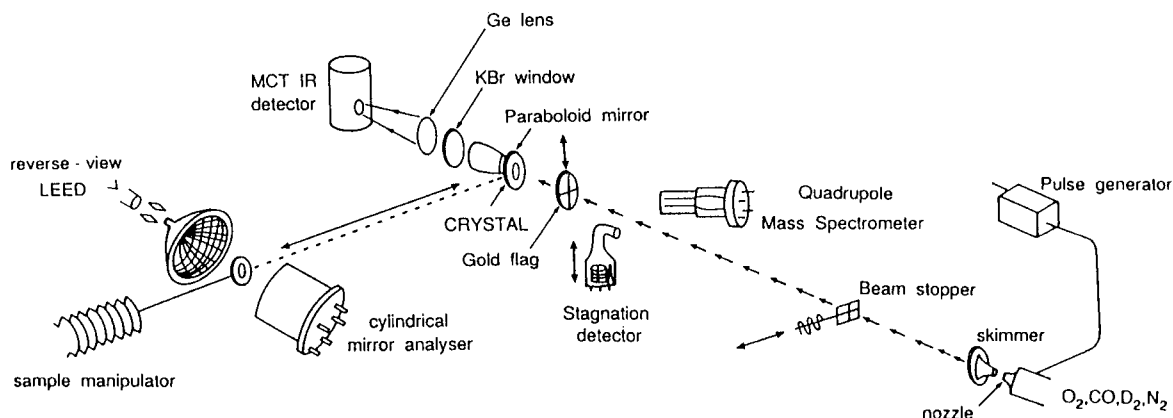


Fig. 6. Sketch of the single-crystal adsorption calorimeter of King et al. [42,43].

means that the calorimeter does not detect any adsorbate reorganization or desorption which may occur between pulses.

Improvements of the prototype version of the calorimeter raised its performance [45]. The detection limit of  $\approx 10 \text{ kJ mol}^{-1}$  enabled the measurements to be carried out with good sensitivity to  $\sim 2\%$  of a monolayer. The systematic error in absolute values of adsorption heats for high sticking probabilities and heats  $> 80 \text{ kJ mol}^{-1}$  did not exceed 6%.

The original single-crystal calorimeter with infrared detection yielded good-quality signals in room-temperature measurements, but it was unsuitable for low-temperature experiments. At low temperatures, however, the change in radiated power resulting from some small temperature rise  $\Delta T$  induced in the crystal is, from the Stefan–Boltzmann law, proportional to  $T^3 \Delta T$  and so becomes rapidly smaller with decreasing temperature. Moreover, the spectral distribution of the infrared radiation shifts to higher wavelengths with decreasing temperature and most of the radiation eventually gets outside the infrared detection window. In order to extend the measurements down to low temperatures, the remote infrared detector was replaced by a pyroelectric  $\text{LiTaO}_3$  sensor [46,47] along the lines pointed out in Section 5. As a result, the measurements eventually may be carried out over the 90–410 K range. The necessary improvements of the pyroelectric version of the single-crystal calorimeter are underway.

The described calorimeter is thus capable of providing, for the first time, heats of both, reversible and irreversible chemisorption on metal single-crystal surfaces of a controlled order and cleanliness as a detailed function of surface coverage, over a wide range of temperatures and sticking probabilities.

Availability of calorimetric heats of adsorption on single-crystal surfaces is of crucial importance for further development of the physics and chemistry of surfaces. A polycrystalline surface exhibits all the adsorption sites of the crystal planes of which it is composed. The heat of chemisorption released in adsorption of a gas dose thus represent an average of the heat on the different surface sites covered by that dose. As a result, the adsorption behavior of different planes, having sites with different coordination numbers and rotational symmetries enabling different adspecies to be formed, is blurred. The

contribution of bonding interactions of the adspecies with the surface and between themselves cannot be unambiguously discerned, and interpretation of experimental data on the atomic scale is therefore difficult. The introduction of this instrument has thus radically enlarged the scope of problems that can be addressed using adsorption calorimetry, and markedly increased the role of this method in the fundamental research of surface physics and chemistry.

On the other hand, construction of such a sophisticated device and its operation are extremely demanding and, hence, all the hitherto completed measurements were carried out using the only available calorimeter at the University of Cambridge.

## 6.2. Results

Since 1991, when the first results were published [48], measurements carried out with the single-crystal calorimeter have provided a wealth of information on the chemisorption and surface reactions in a variety of gas–solid systems. The calorimetric data were mostly combined with the simultaneously measured sticking probabilities.

Much attention was focussed on the adsorption of oxygen, carbon monoxide, nitrous oxide and ethylene on low-index planes of platinum. These systems are of relevance to the function of Pt/Rh car-exhaust catalyst and to further catalytic processes of practical importance [44], as well as to the oscillatory kinetics observed with some of these systems at favourable conditions. Some of the achieved results are described in the following.

While the calorimetric study [26] of ethylene adsorption on polycrystalline Pt films at 300 K suggested that at low coverage prevail on the surface  $\text{C}_2\text{H}_3$  species each blocking two sites, along with dissociated mobile hydrogen adatoms, experiments with Pt{110}- $(1 \times 2)$  [43] and Pt{111} [49] surfaces allowed a more detailed picture to be formulated. On the Pt{111} surface at low coverage, ethylene was proposed to first form ethylidene ( $=\text{CH}-\text{CH}_3$ ) which achieves equilibrium with ethylidyne ( $\equiv\text{C}-\text{CH}_3$ ). Ethylidene was also suggested to arise at higher coverage as a precursor to ethylidyne which cannot be directly formed due to the absence of the needed vacant threefold sites along the domains of islands of out-

of-phase ethylidyne species. Ultimately,  $\pi$ -bound ethylene is formed at the steady state above a monolayer coverage. The average Pt–C bond dissociation energy was estimated to lie in the 225–270 kJ/mol range (a value of 212 kJ was assessed for polycrystalline films [28]).

By contrast, the data measured for the Pt{110}-(1 $\times$ 2) surface pointed to the initial formation of ethylidyne ( $-\text{CH}_2-\text{C}\equiv$ ) followed by the production of ethylidyne and eventually of di- $\sigma$ -bonded and  $\pi$ -bonded non-dissociated ethylene. A single Pt–C bond energy was estimated to decrease from 235 to 214 kJ/mol. Results on further investigations with these systems are to appear in the next Special Issue of the *Journal of Molecular Catalysis*.

From the heat released in catalytic oxidation of CO on a Pt{110} substrate at room temperature [50], the energy carried away by the formed  $\text{CO}_2$  molecules was determined. This energy is in excess of that expected from the substrate temperature. The considerably higher excess energy found when oxygen was dosed to preadsorbed CO compared with that found when CO was reacted with saturated oxygen overlayer, was accounted for by the much greater degree of excitation of the desorbed  $\text{CO}_2$  molecules in the former case due to the channelling of energy from the dissociation of the oxygen molecule via “hot” oxygen adatoms which never thermally accommodated to the surface. A similar study was made with Pt{111} [51].

Adsorption of NO and CO on both, the reconstructed hex and the unreconstructed (1 $\times$ 1) surfaces of Pt{100} [52] showed that the hex surface reverts to the (1 $\times$ 1) structure during adsorption of both gases. The surface energy difference between the two surface structures was obtained by comparing the integral heats of adsorption of CO at half-monolayer coverage. A non-linear growth law for this phase transition accounts for the oscillatory kinetics observed in the NO+CO and CO+O<sub>2</sub> reactions on this surface. NO–NO repulsive interactions are much stronger than CO–CO interactions. The different influence of adsorption at defect sites in the energetics of NO and CO on the hex surface was discussed (Fig. 7).

From the adsorption heats of CO, NO and O<sub>2</sub> on Pt{110} at high coverages, when a steady-state regime was reached, the entropy change of adsorption,

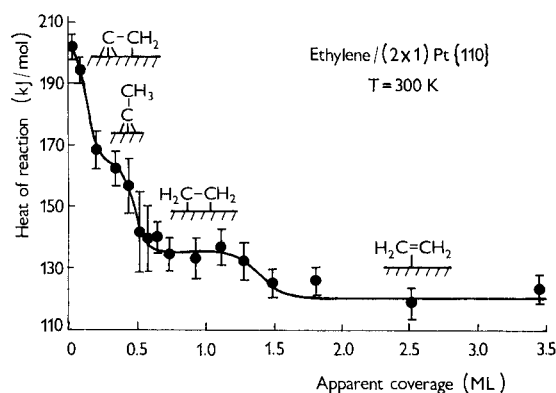


Fig. 7. Heat of reaction of ethylene on Pt{110}-(1 $\times$ 2) as a function of coverage [43]. The error bars indicated are given by the standard deviation of the heats measured in five independent experiments.

the differential entropy of the adspecies and the frequency factor for their desorption were calculated [44].

Nickel is another catalytically important metal whose interactions with gases were intensively studied with single-crystal calorimeter. Heats of chemisorption of oxygen measured on Ni{100}, {110} and {111} at room temperature along with corresponding sticking probabilities were interpreted in terms of initial dissociative chemisorption on different sites of these planes and subsequent growth of oxide films [47]. The rapid fall in the chemisorption heat with oxygen coverage points to strong repulsion between the oxygen adatoms. Chemisorption thus proceeds only up to a coverage at which formation of oxide layer becomes more energetically favourable. Comparison of the heat-coverages curves measured on Ni{100} at 90 K, 300 K and 410 K (the mobility of adlayer increases with increasing temperatures) indicated that the O–O interaction is a local effect due to second-nearest-neighbour repulsions rather than a long-range electronic effect, and that the Ni–O average binding energy increases with improved surface order. The integral heat corresponding to the formation of oxide film (and hence heat of formation, as the reactants are the elements in their standard states) varied widely between the three crystal planes and was on all of them considerably lower than the heat of formation of the bulk NiO. A decline in the heat of

chemisorption with coadsorbed potassium was ascribed either to local K–O attraction compensating for O–O repulsions or to an increase in the surface band electron density by charge transfer from the alkali metal.

Heats of adsorption and sticking probabilities for CO on Ni{110}, {110} and {100} showed differences which were ascribed to different adsorption sites occupied in the adsorption on the particular planes [53].

The large effect of varying amounts of predosed potassium on the heat of adsorption of CO on Ni{100} was accounted for in terms of mechanistic models including electronic and electrostatic processes occurring in the adlayer [54].

Initial heat of adsorption of NO on the Ni{100} surface at room temperature [55] pointed to dissociative chemisorption. In combination with the initial heat for oxygen on the surface, it was possible to predict the heat of dissociative adsorption of N<sub>2</sub>. The O–O, N–O and N–N repulsive interactions were discussed.

The coverage dependence of the heat of adsorption of NO on clean and oxygen-predosed surface Ni{100} suggested that, above a certain critical total adatom coverage, no further NO dissociation is energetically possible due to strong N–O and N–N repulsion. Because of oxygen adatom precoverage, it is possible to increase the interatomic repulsions which energetically control the relative amounts of dissociated and molecularly adsorbed NO. Oxygen may, thus, act as promoter of a catalytic reaction in which molecules of NO are desired (as in NH<sub>3</sub> oxidation to NO), or a poison when N or O adatoms are required (as in the CO+NO reaction) [55].

The coverage dependencies of the differential heats of adsorption of CO on Pd{100} at room temperature were explained by means of a lateral interaction model. The influence of predosed carbon on the heat of adsorption of CO suggests long-range interactions between C atoms and CO molecules. The high initial heat of NO on Pd{100} is assigned to adsorption at defect sites [56].

Even this brief account of the results extracted from experiments using the single-crystal calorimeter shows the power of this method. It is desirable that it should be introduced in further laboratories before long.

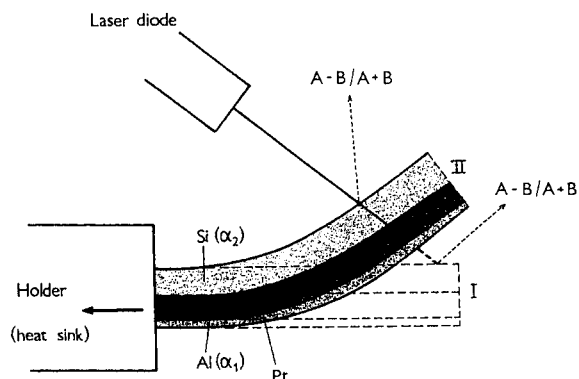


Fig. 8. Scheme of micromechanical calorimeter with optical detection of the cantilever deflection [57]

## 7. Micromechanical calorimeter

A further step in the miniaturization of adsorption calorimeters has been accomplished by designing an instrument for monitoring extremely small heat fluxes on the basis of bimetallic effect (Fig. 8) [57]. A miniature cantilever micromechanically fabricated from Si or Si<sub>3</sub>N<sub>4</sub> ≈0.40 mm long, 0.035 mm wide and 0.0015 mm thick is coated on one side with 500 nm of aluminium. Upon the Al layer is deposited an ≈40 nm thick layer of catalytically active material, for example platinum. The cantilever is fixed in a holder which acts as a heat sink. When a heat-producing process takes place on the catalytic material, the heat is transported along the cantilever towards the holder, giving rise to a temperature gradient. Due to a one-order-of-magnitude higher thermal expansion coefficient of Al compared to Si, the cantilever bends because of bimetallic effect. The bending can be measured using the techniques of atomic-force microscopy. In this way, heat fluxes down to 10<sup>-9</sup> W can be determined corresponding to a sensitivity limit of 10<sup>-12</sup> J. The active area of the sample is of the order of 10<sup>-2</sup> mm<sup>2</sup>, and ≈10<sup>11</sup> molecules are required for its monolayer coverage. Further details can be found in review [1] and references therein.

The micromechanical calorimeter has been so far used to follow the self-sustaining oscillation in the rate of the catalytic reaction of hydrogen and oxygen to water on a platinum surface. The future application of this instrument in surface-science studies depends on how successfully will be solved the estimation of the

adsorbed amount which is required for the determination of the molar heat of the studied surface process.

## 8. Note added in proof

A pyroelectric calorimeter for the measurement of the heat of adsorption of metal vapours on single crystal surfaces has been recently developed, using the pyroelectric properties of a polyvinylidene fluoride film for the temperature sensing (J.T. Stuckless, D.E. Starr, D.J. Bald, C.T. Campbell, *J. Chem. Phys.* 107 (1997) 5547). The first direct calorimetric measurements for metal adsorption on well defined surfaces have been made, giving adsorption and adhesion energies for Pb and Cu on Mo(100) and on surface oxides of Mo(100) and W(100).

A comprehensive review on the femtomole adsorption calorimetry on single crystal surfaces by W.A. Brown, R. Kose and D.A. King will be published in *Chemical Reviews* in the near future.

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