

THE ROLE OF ADSORPTION CALORIMETRY IN THE STUDY OF SURFACE PHENOMENA

G. WEDLER

*Institut für Physikalische und Theoretische Chemie der Universität
Erlangen-Nürnberg, Egerlandstraße 3, D-8520 Erlangen, FRG*

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After a short survey of the development of adsorption calorimetry, the current position of this method is demonstrated in the light of some more recent results. A critical analysis is made of the areas in which adsorption calorimetry could be successfully applied in the future, either alone or, preferably, in combination with other techniques.

Research work in the field of adsorption and heterogeneous catalysis is carried out in order to elucidate both the bonding and the structure of the adsorbed phase and the mechanisms of reactions in the adsorbed layer. In this connection there is a fundamental interest in obtaining thermodynamic information regarding bonding energies and reaction enthalpies. The part which direct calorimetric measurements play in comparison with other methods depends on the relative degrees of reliability, sensitivity and applicability of the various methods.

At first a short survey is given of the development of adsorption calorimetry during the past few decades. Then the current position of adsorption calorimetry is analysed critically and the areas in which this method can be successfully applied are discussed. Finally future perspectives for the use of adsorption calorimetry are given.

The main emphasis will be laid on metals as adsorbents or catalysts.

Previous and current applications of adsorption calorimetry

The first experimental work on adsorption calorimetry dates back to Beebe (1932) [1]. Since this time great efforts have been made to improve the experimental systems in order to allow the use of powders, ribbons, wires or evaporated films as adsorbents, to increase the sensitivity and to improve the reliability. Advances have resulted from the optimisation of the shape of the calorimeter vessel, from more accurate thermal calibration of the cell, and from the automatisation of the data recording. A survey of this development and a critical analysis of the properties of the calorimetric devices is given in the literature [2–5].

The different types of calorimeter used in more recent experimental work are shown in Table 1. The first four types are suitable for investigations with industrial catalysts, while the latter four are used for basic research work. This separation is symptomatic for the present situation of research in the field of adsorption and catalysis. On one hand there are investigations closely connected with in-

Table 1
Different types of calorimeters

Adsorbent	Ultra-high vacuum	Used for study of	Type	Thermometer	References
Powders	no	heat of physisorption and chemisorption	adiabatic (Beebe)	resistance thermometer, thermocouple	[6]
Powders	no	heat of chemisorption, co-adsorption	nearly isothermal (Calvet)	thermocouples	[7]
Supported catalysts	no	kinetics of catalytic reactions	constant-temperature environment	thermocouples	[8]
Supported catalysts	no	heat of adsorption	isothermal	—	[9]
Metal wire	yes	heat of adsorption	adiabatic (Roberts)	adsorbent itself	[10]
Metal film	yes	heat of adsorption	constant-temperature environment	thermocouples	[11]
Metal film	yes	heat of adsorption	constant-temperature environment (Beeck) cylinder	resistance thermometer	[12]
Metal film	yes	heat of adsorption and co-adsorption	constant-temperature environment (Beeck) sphere	resistance thermometer non-inductively fused to the sphere	[13]

dustrial problems of catalysis, using catalysts and conditions as similar to industrial catalytic conditions as possible. On the other hand there are investigations using the ultrahigh vacuum technique, since for over a decade it has been recognized that the obtaining of reproducible data requires clean surfaces. Only such clean surface data can be treated theoretically at the moment.

At present there is a large gap between these two lines of work. As can be seen from Table 2, often the same adsorption system (e.g. Pt/H₂, Fe/H₂ or Fe/CO) has been investigated calorimetrically using both catalysts and films. The results obtained differ largely, especially concerning the coverage-dependence of the differential heat of adsorption. This must be due to differences in the chemical composition, cleanliness or structure of the surface of industrial catalysts and evaporated films or polycrystalline wires.

Table 2
Comparison of heats of adsorption measured with catalysts
and wires or films

Absorbent	Type of Calorimeter	Temperature	Initial heat of adsorption in kJ mole^{-1}	Decrease of q with coverage	References
Silica supported Pt	isothermal	Pt/H ₂	88.0	non-linear, maximum of q at $\theta =$ $= 0.35$	[10]
		300 K			
Polycrystalline Pt filament	thin wire (Roberts)	273 K	104.5	step-like, steep fall at $\theta = 0.6$	[22]
Polycrystalline Pt film	metal film (Beeck)	298 K	80.0...94.5*	linear	[13]
Reduced magnetite	Beebe	Fe/H ₂ 293 K	83.5	linear	[7]
Polycrystalline Fe film	metal film (Beeck)	273 K	97.0	step-like, 3 steps	[23, 42]
Reduced magnetite	Beebe	Fe/CO 293 K	113.0	convex	[7]
Polycrystalline Fe film	metal film (Beeck)	273 K	153.0	step-like, 3 steps	[24]

* Depending on extent of surface contamination

In order to find a solid basis giving reproducible results, very simple systems have been studied using evaporated films or wires as adsorbents. Such systems which have been intensively investigated under ultrahigh vacuum conditions are e.g. Ni/H₂ [5, 25], Fe/H₂ [23, 42], Pt/H₂ [13, 22], Mo/H₂ [48], W/H₂ [11, 26], W/N₂ [27], Ni/CO [5, 49] or Fe/CO [24]. Nowadays it is possible to perform calorimetric determinations of differential heats of adsorption with a high degree of reproducibility. As an example, in Fig. 1 the coverage-dependence of the differential heat of adsorption of H₂ on five different Ni films prepared under the same conditions is shown. The experiments were performed by different co-workers. Such a well-established calorimetric system even allows the measurement of isotopic effects [42], as can be seen from Fig. 2. The differences in the heats of adsorption of H₂ and D₂ can be traced back to differences in the zero-point energy.

Present efforts are being directed to the removal of ambiguities regarding the evaluation of the heat of adsorption from the measured quantities, especially from the "calorimetric curves", i.e. the curves of temperature against time. If the adsorption does not occur with a very high rate, the kinetic order and the rate of the adsorption process strongly influence the calorimetric curve. Some work in

this direction has already been done [4, 13, 15, 16], but there are still many unsolved problems remaining.

The experiments just mentioned were performed under conditions far removed from catalytic relevance. There is, however, a trend to narrow the gap since not only very simple systems are being studied under UHV conditions but also systems in which the adsorbate is a hydrocarbon, an olefine, an acetylene [28–30] or a mixture of different gases [23, 32, 43]. Another important step in this direction would be to study calorimetrically the adsorption on alloy films or on metal films which are reproducibly contaminated.

Despite the significant successes of adsorption calorimetry and the improvements in the details mentioned above, interest in the application of calorimetry has been decreasing recently due to the introduction of new and the sophistication of older physical methods. These either provide an indirect determination of heats of adsorption or, as with the electron spectroscopies, allow a direct experimental determination of the energies of the chemisorption orbitals.

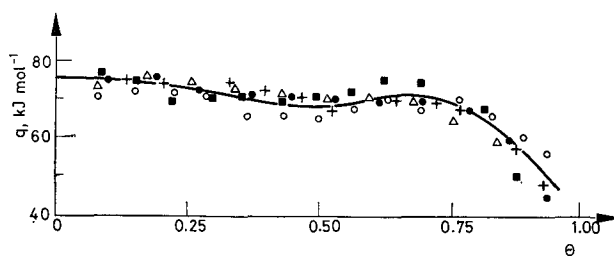


Fig. 1. Reproducibility of the differential heat of adsorption of H_2 on Ni films at 273 K as a function of coverage θ

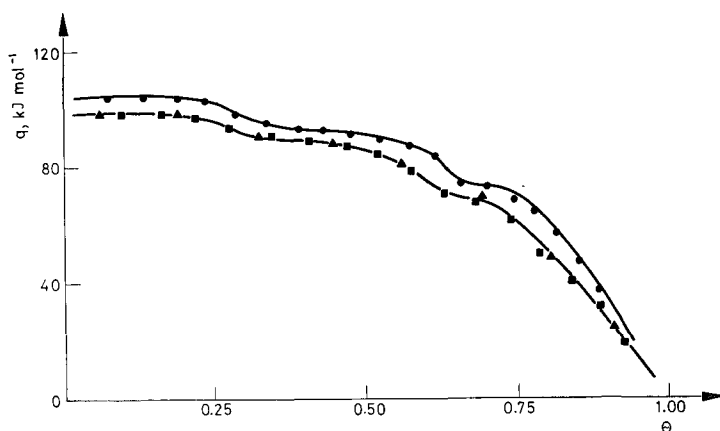


Fig. 2. Differential heats of adsorption of H_2 (■, ▲) and D_2 (●) on Fe films at 273 K as a function of coverage

In former years calorimetric measurements were carried out in order to characterize both the bond between the adsorbed species and the adsorbent and the lateral interactions in the adsorption layer. Nowadays heats of adsorption and their dependence on coverage are very often determined as isosteric heats of adsorption, since the reliability of measurements of low pressures (10^{-7} torr) has been improved and indirect methods for the determination of coverages are available. The measurement of adsorption isosteres with the aid of surface potential determinations using the vibrating capacitor method [17] may be given as an example. In general these values agree very well with those determined calorimetrically [5]. Nevertheless, it is desirable to check such values by calorimetric measurements, since a prerequisite for the determination of isosteric heats of adsorption is the establishing of the thermodynamical equilibrium. The measured pressure, however, is not always the equilibrium pressure, especially in the low-pressure range. Due to experimental difficulties, adsorption calorimetry cannot as yet be applied to single-crystals. In this regard, attempts to produce films exposing predominantly one particular surface orientation are of great interest [18–21].

Although the importance of adsorption calorimetry has been reduced in its original field of application, there are some new areas where adsorption calorimetry will be used successfully.

As already mentioned above, the rate of liberation of the heat of adsorption depends on the rate of adsorption, which may occur in one step or in a sequence of different steps, e.g. in the case of a dissociative adsorption. If the adsorption or a subsequent process in the adsorption layer is not a very rapid process, the rate of change in temperature of the calorimeter is markedly affected by the rate of the slowest step. Therefore, it is sometimes possible to draw conclusions concerning the mechanism of adsorption from the measured temperature-time curves. Since the determination of the kinetics of adsorption is a general problem which very often cannot be solved by employing other techniques, calorimetric measurements can be helpful in this respect.

Up to now no quantitative evaluations are available. But there are some qualitative observations: Carbon monoxide is known not to decompose on Ni, but is known to decompose on Fe to some extent at room temperature. If one compares the calorimetric curves for the two systems under identical experimental conditions, one sees that the cooling constant for Fe/CO is considerably smaller than that for Ni/CO (Fig. 3) [24], which is nearly identical with that determined by the calibration of the calorimeter by the pulse method [14]. The decomposition of the carbon monoxide slowly releases the extra heat of adsorption of the decomposition products, whereby the cooling after the initial release of the heat of adsorption of molecular carbon monoxide is partially compensated. From the rapid initial rise in temperature the heat of adsorption of molecular CO is calculated. An exact evaluation of the cooling curve should provide the kinetics of the decomposition process.

During the past few years calorimetric measurements have been successfully applied to the study of the adsorption of gas mixtures and to the sequential adsorp-

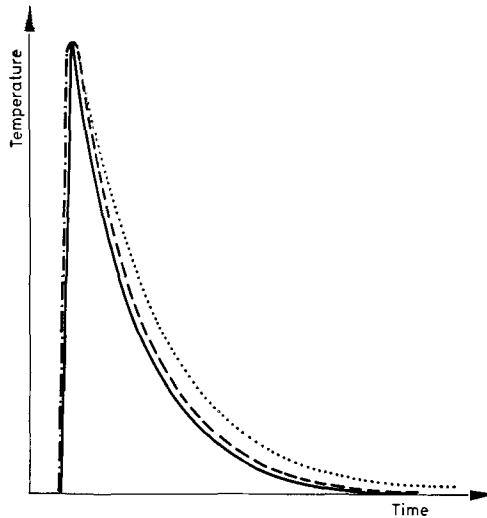


Fig. 3. Calorimeter curves plotted after applying a 5 s pulse of electric current flowing through the evaporated film (—), after CO adsorption on a Ni film (---), and after CO adsorption on an Fe film (...)

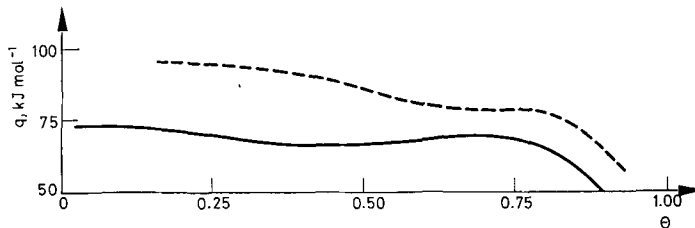


Fig. 4. Heats of adsorption of H_2 on a clean Ni film (—) and on a Ni film after preadsorption of CO (--- $\theta_{CO} = 0.1$)

tion of different gases [8, 31–33]. In such cases the indirect determination of coverages (e.g. by surface potential measurements) is either impossible or at least uncertain, so that there is almost no chance of determining isosteric heats of adsorption. Direct calorimetric measurements, however, have proved to be sensitive enough to reflect mutual interactions which cannot be observed by other “modern” methods such as UPS. Ertl et al. [34] investigated the co-adsorption of H_2 and CO on Ni(111). The UPS spectrum of the co-adsorption layer was merely a superposition of the individual spectra of H_2 and CO on Ni(111). The LEED pattern, however, showed an ordered structure for the co-adsorption, indicating an interaction energy. An increase in the heat of adsorption of H_2 on a Ni film partially precovered with CO compared with the heat of adsorption on a clean film is indeed found calorimetrically (Fig. 4) [32].

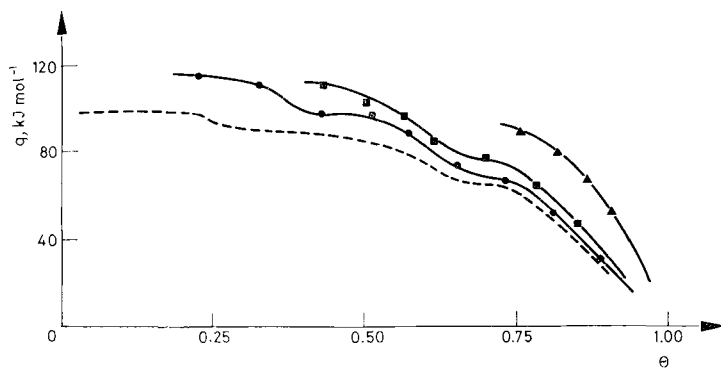


Fig. 5. Heats of adsorption of H_2 on a clean Fe film (— — —) and on an Fe film after preadsorption of CO up to $\theta_{CO} = 0.18$ (●), $\theta_{CO} = 0.42$ (■) and $\theta_{CO} = 0.73$ (▲)

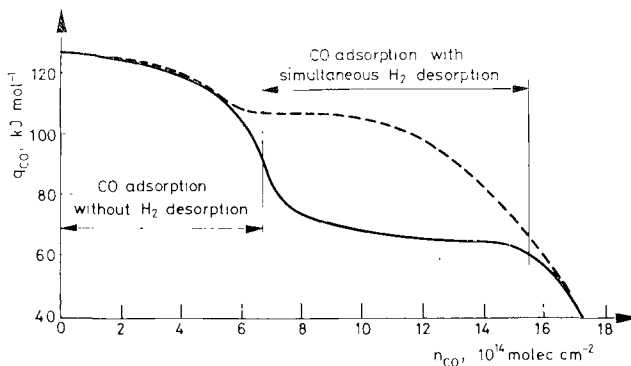


Fig. 6. Heats of adsorption of CO on a clean Ni film (— — —) and on a Ni film after preadsorption of H_2 up to 5×10^{11} molecules H_2 cm^{-2} (—)

Similar observations have been made with the system $Fe/CO + H_2$. In Fig. 5 [43] the dashed line shows the coverage-dependence of the differential heat of H_2 adsorption on a clean Fe film. The solid curves were obtained for H_2 adsorption on Fe films precovered with CO to 18%, 42% and 73% of a monolayer. The higher the precoverage is, the larger is the effect. The increase in the heat of adsorption of H_2 is not restricted to an amount of H_2 comparable with the amount of preadsorbed CO, but is observed up to the completion of a monolayer. This clearly indicates that the increase in the heat of adsorption cannot be traced back to the formation of a stoichiometric adsorption complex between hydrogen and carbon monoxide, but must be due to long-range interactions.

Since the heats of adsorption of CO and H_2 on the transition metals differ largely from each other, it is also possible to study calorimetrically displacement effects, e.g. the displacement of preadsorbed H_2 by CO from Ni. The dashed line in Fig. 6 shows the heat of adsorption of CO on a clean Ni film, and the solid

line that observed after a precoverage with 5×10^{14} molecules $\text{H}_2 \text{ cm}^{-2}$. It is clearly seen that up to $n_{\text{CO}} \approx 6 \times 10^{14}$ molecules CO cm^{-2} the CO is adsorbed as on a clean Ni film. Between $n_{\text{CO}} \approx 6 \times 10^{14}$ and $n_{\text{CO}} \approx 16 \times 10^{14}$ molecules CO cm^{-2} the measured "heat of adsorption" is markedly lower since H_2 is desorbed, as can be seen from the analysis of the gas phase. The measured q values are the differences between the heat of adsorption of CO and the heat of desorption of H_2 , regarding the relative amounts of adsorbed and desorbed gases (nearly two CO molecules are required to displace one H_2 molecule into the gas phase) [32]. The value of such a discussion is appreciably increased, when simultaneously with the calorimetric measurement other methods are applied [32] (see below).

Calorimetric measurements of co-adsorption and replacement effects form a link with the measurement of heats of reactions during heterogeneous catalysis, an even more complicated task. Such experiments must not be confused with the microcalorimetric studies performed to obtain kinetic data, e.g. by Firth et al. [9, 35–37]. These are yet another interesting application of calorimetry.

It cannot be denied that much work remains to be done before the accuracy of the thermodynamic data obtained calorimetrically with complicated adsorption systems reaches the desired level. An experimental difficulty common to all measurements in adsorption calorimetry should be mentioned. Independent of the type of calorimeter used, a very high degree of temperature stability is needed. This demand at present restricts the range of measuring temperatures to values at or below room temperature, 77 K, 90 K, 178 K, 273 K, and 298 K being the most frequently used temperatures.

The combination of adsorption calorimetry with other methods

Experience in adsorption studies has shown that the employment of one technique alone is not to be recommended [5]. Only when the results obtained with different methods are compared can reliable conclusions be drawn. Furthermore, it is essential that the different measurements are performed under exactly the same experimental conditions. There is, however, a general problem existing in the necessity of a sudden addition of a known dose of gas which has to be adsorbed quantitatively by the adsorbent and not by other parts of the apparatus. A known dosing can be achieved by adding the gas from a source or a large storage bulb via a pipette system or by admitting the gas from break-seal ampoules. As a consequence of the high adsorption capacity of baked metal in contrast with baked glass, it is not possible to carry out measurements with thin film calorimeters in the nowadays common all-metal vacuum systems. Calorimetric measurements can only be performed in all-glass systems.

Despite the fact that the design and construction of a calorimeter cell largely restricts the simultaneous application of other methods, there are some quantities which can be determined alongside the heat measurements.

The determination of the adsorbed amount, and therefore of the coverage, is a prerequisite to calorimetric measurements. Furthermore, the measurement of the pressure can easily be carried out by means of ionisation gauges with a sufficiently low pumping speed. Therefore, it is possible to determine adsorption isotherms, provided that the measured pressure is the equilibrium pressure (see above). From the kind of adsorption isotherm, further conclusions can be drawn concerning the state of the adsorbed species [5]. There is, however, the danger of a misinterpretation if the pressure range covered by the adsorption isotherm is not large enough.

During the past few years thermal desorption experiments have been applied successfully to the detection of the different states of the adsorbed species [5] and to the determination of adsorption and desorption energies. Since the calorimeter is well suitable also for temperature measurements over a wide range, thermal desorption experiments can easily be carried out when the calorimetric measurements have been performed. It is preferable then to use a mass-spectrometer to measure the partial pressure of the desorbing species. Figure 7 shows as an example the desorption spectrum of CO from an Fe film carried out with a spherical thin film calorimeter. The pressure was measured by means of a Topatron mass-spectrometer (Leybold, Köln, F. R. G.) which can easily be attached to an all-glass UHV system. The diagram clearly shows two different states of CO, desorbing at temperatures of about 370 K and 660 K.

If the adsorption is carried out on evaporated metal films, the change in resistance of the film due to the adsorption can be determined simultaneously with the heat of adsorption [5, 15]. These changes in resistance have proved to be a

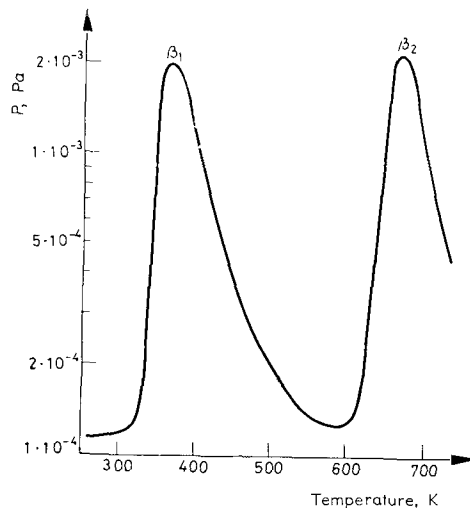


Fig. 7. Thermal desorption of CO from an Fe film, measured by means of a spherical thin film calorimeter

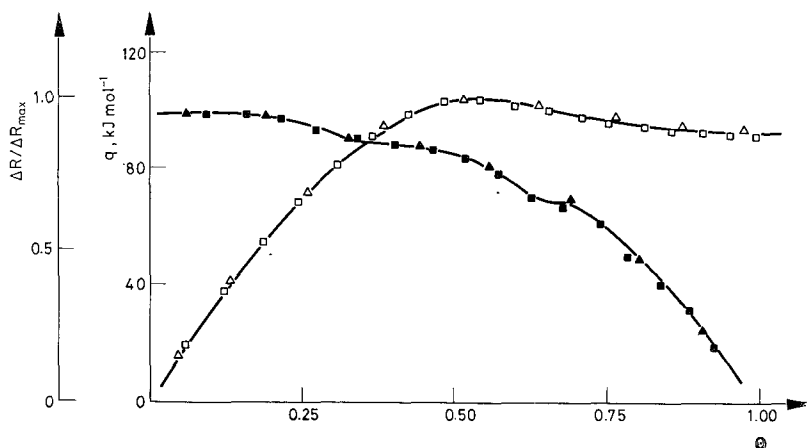


Fig. 8. Differential heats of adsorption (■, ▲) of H_2 on Fe films at 273 K and relative changes in resistance (□, △) as a function of the coverage

very sensitive indication of the state of the adsorption system [5, 18, 41]. This is demonstrated in Fig. 8, which shows the coverage-dependence of the differential heat of adsorption and the coverage-dependence of the relative change in resistance for the system Fe/ H_2 at 273 K.

Therefore, such resistance measurements are well suited to the comparison of experiments performed in cells of different shapes. Moreover, these measurements are also a convenient means to compare, contrast and combine the results of calorimetric measurements with data obtained in adsorption experiments using other methods in other kinds of systems, e.g. all-metal systems, such as surface potential measurements [24], ellipsometric studies [44], measurements of low-energy diffraction [21, 45], X-ray diffraction [21] or Auger electron spectroscopy [21, 45], as has already been shown. There are no difficulties to include in such a comparison via resistance measurement experiments using electron energy loss spectroscopy [5, 45], the photoelectron spectroscopies UPS and XPS [5, 45], appearance potential spectroscopy [5, 45] or electron-induced desorption [46] and photodesorption [47].

Future perspectives for the use of adsorption calorimetry

Adsorption calorimetry is a rather complicated method. Although the apparatus for such calorimetry is much less expensive than that required for the newer physical techniques such as LEED, UPS, XPS, SIMS, etc., it cannot be bought; it must be "home-made", at least when the calorimeter systems summarized in the lower part of Table 1 are considered. Furthermore, the time required to measure differential heats of adsorption by calorimetry is much longer than the time usually required by other methods of surface study. These factors tend to restrict the widespread application of adsorption calorimetry.

At present there is a trend leading away from surface chemistry to surface physics, from adsorption on polycrystalline material to adsorption on single-crystals. As a consequence, the importance of adsorption calorimetry in the study of the adsorption of pure gases on extremely clean surfaces is decreasing in comparison with other methods. There is, however, the demand for a narrowing or even closing of the expanding gap between the physics of surface phenomena and the chemistry of industrially relevant heterogeneous catalysis.

Further improvements of adsorption calorimetry, especially using polycrystalline films of high cleanliness, alloy films or metal films "promoted" in a known and reproducible manner, will be helpful in solving problems which lie exactly in the gap. Such problems include the adsorption of mixed gases, displacement reactions, investigations of attractive and repulsive interactions in the adsorbed layer, kinetics of processes in the adsorbed layer having time constants of the order of a minute, and the distinction between adsorption and absorption of gases. It is essential that the path inwards from the borders of the research gap between surface physics and heterogeneous catalysis be taken in small steps to prevent a loss of contact with the reliable basis of knowledge gained with simple systems in both the surface physics and industrial catalyst regions.

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RÉSUMÉ — Après une brève revue du développement de la calorimétrie d'adsorption, on montre la position actuelle de cette méthode à la lumière de quelques résultats plus récents. On donne une analyse critique des domaines dans lesquels la calorimétrie d'adsorption pourrait être appliquée avec succès, seule ou, de préférence, en combinaison avec d'autres techniques.

ZUSAMMENFASSUNG — Nach einem kurzen Überblick über die Entwicklung der Adsorptionskalorimetrie wird die augenblickliche Bedeutung dieser Methode an Hand einiger neuerer Ergebnisse demonstriert. Es wird kritisch analysiert, in welchen Gebieten die Adsorptionskalorimetrie in Zukunft erfolgreich eingesetzt werden kann, sei es allein, oder zweckmäßigerweise in Verbindung mit anderen Techniken.

Резюме — После краткого обзора развития адсорбционной калориметрии наглядно показано существующее положение этого метода в свете некоторых более недавних результатов. Проведен критический анализ областей, в которых адсорбционная калориметрия может быть использована в будущем или как единственный метод, или в комбинации с другими методами.