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Abrasion: A New Powerful Technique For Ultraclean Investigation of the Gas/Solid Interface

Concept and Model

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Abstract. It is shown that a set of isothermal adsorption measurements on 'fresh' surfaces resulting from abrasion in UHV, is in principle sufficient to give the controlling parameters of both adsorption and desorption reactions, provided a convenient and realistic model for their interpretation is designed in such a way as to account for both adsorption and desorption fluxes.

A combined use of abrasion with the model may constitute a new, easy and reliable technique for ultraclean investigation of the gas/solid interface.

1. Introduction

This paper comments critically on the combined use of a method for creating 'fresh' surfaces – surfaces obtained by fracture – in UHV by abrasion and a model for the treatment of the resulting adsorption data. The outlined procedure is shown to constitute an ultraclean, easy and reliable technique for the investigation of gas/solid interactions. In a second paper [1], the application of this new technique is illustrated for the case of hydrogen adsorption on nickel.

When setting up an experiment for investigation of gas/solid interactions, one of the great problems to overcome is the cleanliness, especially that of the surface of the sample. It was fully realized, since the use of Auger spectroscopy started to become a routine, that the standard cleaning procedures used up to that time were far from providing clean surfaces, whatever the material. Once it is acknowledged that minute traces of surface impurities can drastically affect a reaction process (catalysis gives many examples), the divergence of the results obtained with apparently quite similar gas/surface experiments is partly explained simply by the lack of a suitable, efficient, and reproducible cleaning procedure.

Since the cleanest surfaces are *fresh surfaces*, an experimental technique was devised in order to use fresh surfaces, as obtained by abrasion, for the investigation of gas/solid interactions.

To keep the pristine ultraclean fresh surface free from any contamination during experiments, the technique has to be of the cleanest and most straightforward type. Namely it consists in exposing the fresh surface to a gas pressure only for a short time in order to induce gas adsorption.

Such *adsorption experiments* do not involve perturbations due to changes in surface temperature and the associated diffusion of bulk impurities to the surface or effects resulting from electron bombardment, high electric field, etc.

For the evaluation of the adsorption curves resulting from the application of the abrasion technique, a simple but fairly general model was designed in such a way to account for the desorption flux which is always associated to any adsorption reaction. Therefore the model is capable of providing the controlling parameters of both the adsorption *and* desorption reactions. The proposed model for the treatment of adsorption data can also be used independently of abrasion; conversely adsorption data obtained by abrasion can also be interpreted independently of the model [2].

Depending on the nature of the sample and the conditions for abrasion, the resulting fresh surfaces can have a variety of structures from ordered – polycristalline – to highly disordered. It can either behave like 'normal' atomically clean surfaces or offer unique features of great fundamental and practical interest. The abrasion technique has therefore a twofold application. It can be considered either as a new complement to the standard techniques for investigation of the gas/solid interface or as a technique for simultaneous creation of a fresh surface and characterization of its peculiar properties.

2. The Technique of Abrasion

The device required for the creation of a fresh surface by abrasion is basically composed of a cutting tool which can be positioned and moved against the surface of the sample, from outside the UHV chamber (see Fig. 1). The shape and nature of the fresh surface (amorphous furrow, polycristalline cut, etc.) depend on the brittleness or ductility of the sample, the relative hardness of the tool with respect to that of the

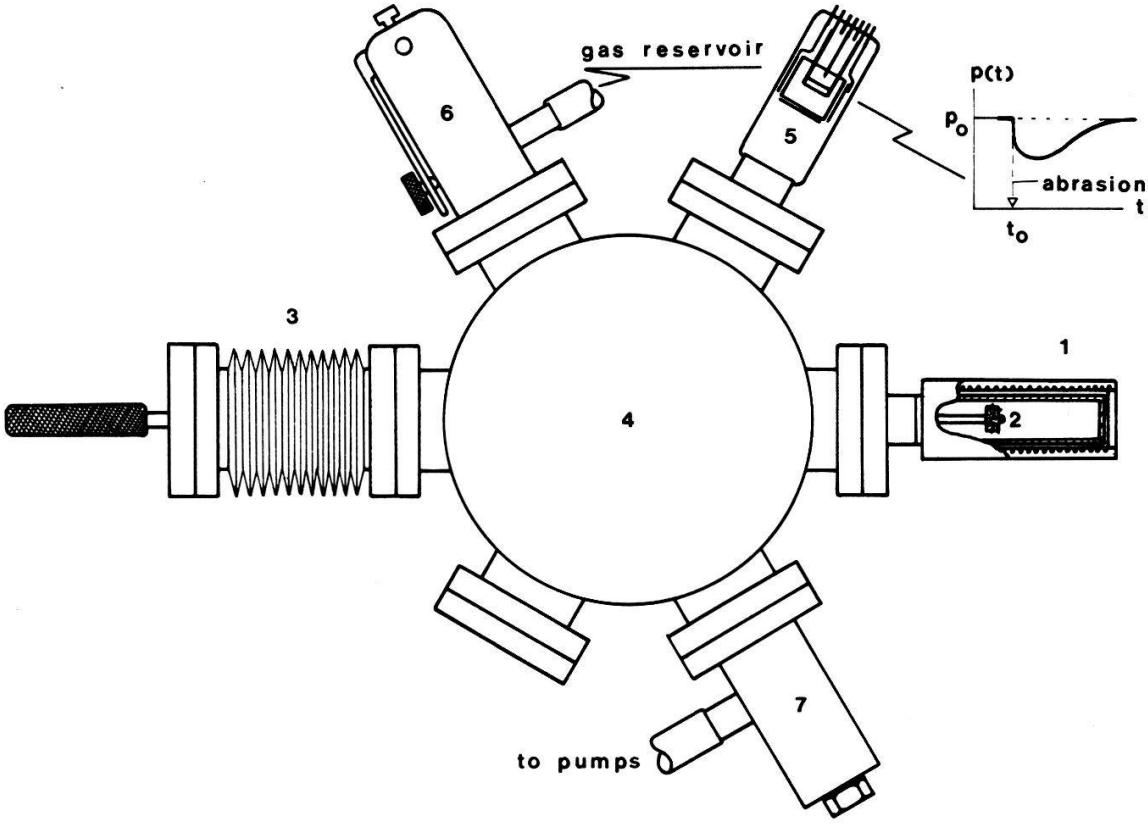

Figure 1
Schematic experimental set-up. 1, Exploded view of the sample (tube), including furnace, etc.; 2, abrasing tool; 3, actuator for abrasing tool; 4, UHV chamber; 5, mass spectrometer or pressure gauge; 6, leak-in valve; 7, pumping valve.

sample, and on such parameters as the geometrical shape of the tool, the contact pressure, the stroke, etc.

The advantages of the technique of abrasion[1]) for the study of adsorption and desorption reactions are outlined below.

Abrasion *provides an ultraclean surface* because none of the usual sources of contamination – diffusion of bulk impurities to the surface, adsorption of gas impurities onto the surface – can play a role for a surface created immediately prior to its use. The only possible contribution comes from the tool – usually diamond or alumina – if not plated with the same material as the sample, or entirely made of this material.

Abrasion is essentially *isothermal*, with a possible sharp and short temperature rise[2]), which may occur just below the cutting tool. Therefore, all the parameters, mainly the rate constant for the reactions of adsorption and desorption, are measured at constant temperature. These seem to be the only experimental conditions under which these parameters have a well-defined physical meaning and can be compared with the expressions given by the theory of reaction rates. Moreover, the temperature of the fresh surface is *homogeneous*, because the fresh surface can be created only on a small portion of the sample; there is no problem of heat conduction due to a sample holder.

Abrasion can be *repeated indefinitely* under the same conditions.

Abrasion is a *rapid process* without long transient (unlike the somewhat related 'hot filament' technique for inducing adsorption).

Abrasion is, however, inconvenient for providing surfaces of known crystallographic orientation. Depending on the ductility of the sample, the freshly abraded surface can have a variety of structures, from ordered (polycristalline) to highly disordered ('amorphous', heavily deformed structure). This feature does not appreciably detract from the merits of the technique, even when used as a complement to standard techniques of gas/solid interactions studies, for the following reasons:

— the surface structure obtained by abrasion is more like that of the usual surfaces met in the *real* world, in catalysis for example, than that of a single crystal face;
— a near perfect crystallographic surface structure *on the atomic level* – the only scale relevant for adsorption – is extremely difficult to obtain, and impossible to confirm experimentally;
— when ideally disordered (as a fresh Ni surface seems to be [1]), a fresh surface can be as energetically uniform – homogeneous – as an anticipated single crystal plane.

The roughness factor can be higher than one, so that the apparent area A' can be smaller than the true area A. Depending on the application, a ratio A/A' greater than one could be advantageous. Determination of both areas A and A' is required for every application.

Accuracy and reproducibility of the grooves cut by this method depend on the degree of sophistication of the mechanical device, and will be the best with an automatic positioning and actuating system. However, in cases where the reproducibility of A', A and A/A' between similar abrasions is difficult to ensure, owing to a primitive mechanical device, a mathematical processing of the data can be applied to circumvent this lack of reproducibility [1].

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[1]) These comments concern to some extent all techniques of creation of fresh surfaces such as cleavage, grinding, fracture, ion bombardment without annealing, film evaporation, etc.

[2]) For nickel, this temperature rise was found to be limited to 50°C for some milliseconds and to decay below 1°C within one second.

3. The Model for the Treatment of Adsorption Data

Instead of ignoring the contribution of the reaction of desorption during adsorption experiments, in the hope that this simplification is valid, a model has been developed which deliberately takes the desorption flux into account in the opposite hope that its contribution will be large enough to be accurately measured. It relates the net adsorption flux $d\sigma/dt$ to the adsorption and desorption fluxes according to the following expression:

$$\frac{d\sigma}{dt} = k_A(T) f(p) g(\sigma) - k_D(T) h(\sigma)$$

where: k_A = rate constant for the adsorption reaction

$$= k_{A0} \exp\left\{\frac{-E_A}{RT}\right\} (s^{-1}) \text{ with}$$

k_{A0} = pre-exponential factor
E_A = activation energy for the adsorption reaction;
k_D = rate constant for the desorption reaction

$$= k_{D0} \exp\left\{\frac{-E_D}{RT}\right\} (s^{-1}) \text{ with}$$

k_{D0} = pre-exponential factor
E_D = activation energy for the desorption reaction;
$f(p)$ = dependence of the adsorption on the pressure p in the gas phase (order of the adsorption reaction with respect to pressure); for small variation of pressure, $f(p) \cong f(p_0)$ (see 5.1);
$g(\sigma)$ = dependence of the adsorption on the availability of the free adsorption sites expressed in terms of surface population density σ (order of the adsorption reaction with respect to free sites);
$h(\sigma)$ = dependence of the desorption on the surface population density (σ) (order of the desorption reaction).

The fluxes are therefore normally expressed as the product of a rate constant times a function of the concentrations of the reactants.

The model is valid if:

— the separation of the variables p, T and σ is realistic, an assumption which has to be discussed for every application;
— the desorption does not depend on the pressure in the gas phase (Eley–Rideal processes excluded).

Apart from these two restrictions *a priori*, the model is quite general and involves only unknown functions, namely k_A, k_D, $f(p_0)$, $g(\sigma)$, $h(\sigma)$, to be determined.

4. Procedures for Experimentation and Calculation

A typical experimental set-up is illustrated in Figure 1, for the case of a tubular sample which can be lodged in a cylindrical furnace.

The standard experimental procedure consists of abrading, at constant temperature, the surface of the sample under a dynamic equilibrium pressure $p(t) = p_0$ of one gas (or more than one gas for co-adsorption) and in recording the change of pressure $p(t)$ resulting from the adsorption of the gas on the freshly created surface.

The procedure is repeated for different pressures at constant temperature and for different temperatures.

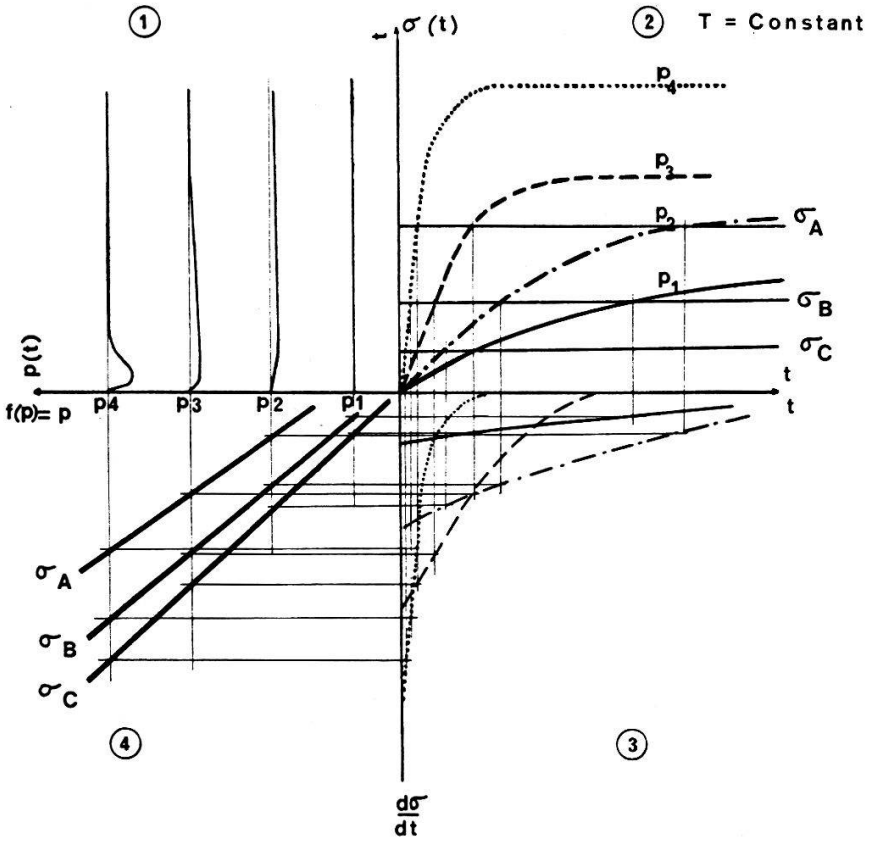

Figure 2

Procedure for the treatment of isothermal adsorption data. ① Family of adsorption curves $(p_{0i} - p(t))$ for different equilibrium pressures p_{0i}; ② resulting surface population curves as a function of time $(\sigma(t))$; ③ resulting surface population rate curves as a function of time $(d\sigma(t)/dt)$; ④ resulting dependence of $d\sigma/dt$ as a function of p_{0i} for different surface populations $(d\sigma/dt = k_A p_{0i} g(\sigma) - k_D h(\sigma))$.

The procedure for the extraction of the unknown functions k_A, k_D, $f(p_0)$, $g(\sigma)$, $h(\sigma)$, from the sole experimental knowledge of $d\sigma/dt$[3]) and p_0 is based on the fact that the model expresses a linear dependence of $d\sigma/dt$ as a function of $f(p_0)$, when σ and T are maintained constant.

From the family of adsorption curves $p_0 - p(t)$ recorded at constant temperature T_i, each one under a different equilibrium pressure p_{0j}, the corresponding family of $\sigma(t)|_{T_i, p_{0j}}$ curves giving the surface population as a function of time is derived (see Fig. 2). When the family of $\sigma(t)|_{T_i, p_{0j}}$ curves is intersected by another family of horizontal lines $\sigma_k = \text{constant}$, the slopes of the $\sigma(t)|_{T_i, p_{0j}}$ curves, measured at the intersections with the $\sigma_k = \text{constant}$ lines, provide sets of values $d\sigma/dt|_{T_i, p_{0j}, \sigma_k}$ versus p_{0j}, at constant temperature T_i and surface population σ_k, for different values of σ_k.

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[3]) $\dfrac{d\sigma}{dt} = \dfrac{-K}{A}\left[V\dfrac{dp}{dt} + S(p(t) - p_0)\right]$. See Ref. [3].

The whole procedure can be repeated for different temperatures. Once the values of $d\sigma/dt|_{T_i, p_{0j}, \sigma_k}$ are known, the first of the unknown functions, namely $f(p_0)$, can be determined by choosing f so that the linear dependence between $d\sigma/dt$ and $f(p_0)$ holds. As $f(p_0)$ often is a power function p_0^n, the determination is facilitated by plotting $\log d\sigma/dt$ as a function of $\log p_0$, which yields an asymptotic straight line in the range where the desorption term is negligible, whose slope n represents the order of the reaction of adsorption with respect to the pressure. Although n is frequently one, this value should not be assumed *a priori* without due verification as is often done in the literature.

Once $f(p_0)$ is determined, $d\sigma/dt$ can be plotted linearly versus $f(p_0)$, which yields a straight line with slope $k_A g(\sigma)$ and intercept at the origin $k_D h(\sigma)$.

The dependence of $k_A g(\sigma)$ as a function of σ at constant T gives the function $g(\sigma)$, i.e. how the reaction of adsorption proceeds. Similarly, the dependence of $k_D h(\sigma)$ as a function of σ at constant T gives the function $h(\sigma)$, i.e. the order of the desorption reaction. The same terms $k_A g(\sigma)$ and $k_D h(\sigma)$, when plotted as a function of T at constant surface population, give the activation energy for the adsorption and desorption reactions, respectively.

The concept was found not to be original, although to our knowledge it has never been fully exploited. It appeared for the first time in a paper by Becker and Hartmann [4], where it is briefly outlined as a possible exploitation of their results of adsorption by the 'hot filament' technique. Ehrlich mentioned the reference in a review paper [5]. Later, in a short note, Amenomiya [6] (without reference either to the Becker and Hartman or to the Ehrlich articles) attempted to apply it to the results of high pressure adsorption of H_2 on alumina, but without much success owing to inadequate experimental data.

5. Some Comments

5.1. The procedure does not require the dynamic equilibrium pressure p_0 to be a constant. If the change $p_0 - p(t)$ in pressure due to adsorption is too large (as compared with p_0) to be neglected, the proper value of $p(t)$ has to be used in connexion with the slope $d\sigma/dt(t_l)|_{T_i, p_{0j}(t_l), \sigma_k}$, instead of the constant value p_{0j}.

From another point of view, the extent of the pressure change has to be limited in order to prevent the occurrence of stray effects due to interactions of the gas with the gauge, the walls of the UHV chamber, etc. By electronic means (zero suppress function) and high quality electronics, it is easy to limit the pressure change to within 3 to 5% of p_0, while keeping full accuracy for the recording of the adsorption curve.

5.2. The procedure is still valid if the activation energy for adsorption E_A and/or desorption E_D is a function of the surface population σ and gives the dependence $E_A(\sigma)$ and $E_D(\sigma)$.

5.3. The conclusions which can be drawn are highly reliable, because they result from calculations involving a *set* of experiments, which can be taken as large as desirable, and not from a single experiment.

5.4. Each experiment of the set involves a new fresh surface and cannot suffer from memory effects.

5.5. The relevant parameters from the reaction of desorption are derived from adsorption experiments, i.e. from a type of experiment which is much cleaner than the desorption experiments.

5.6. The intersections of the straight lines $d\sigma/dt$ versus $f(p_0)$ with the abscissa represent conditions where $d\sigma/dt = 0$, i.e. equilibrium. Comparison of these points with the isotherm curves provides an independent check of validity for the model.

5.7. For isothermal desorption (see Fig. 3), i.e. thermal desorption induced by a step function heating programme, the model must apply *mutatis mutandis*. $d\sigma/dt$,

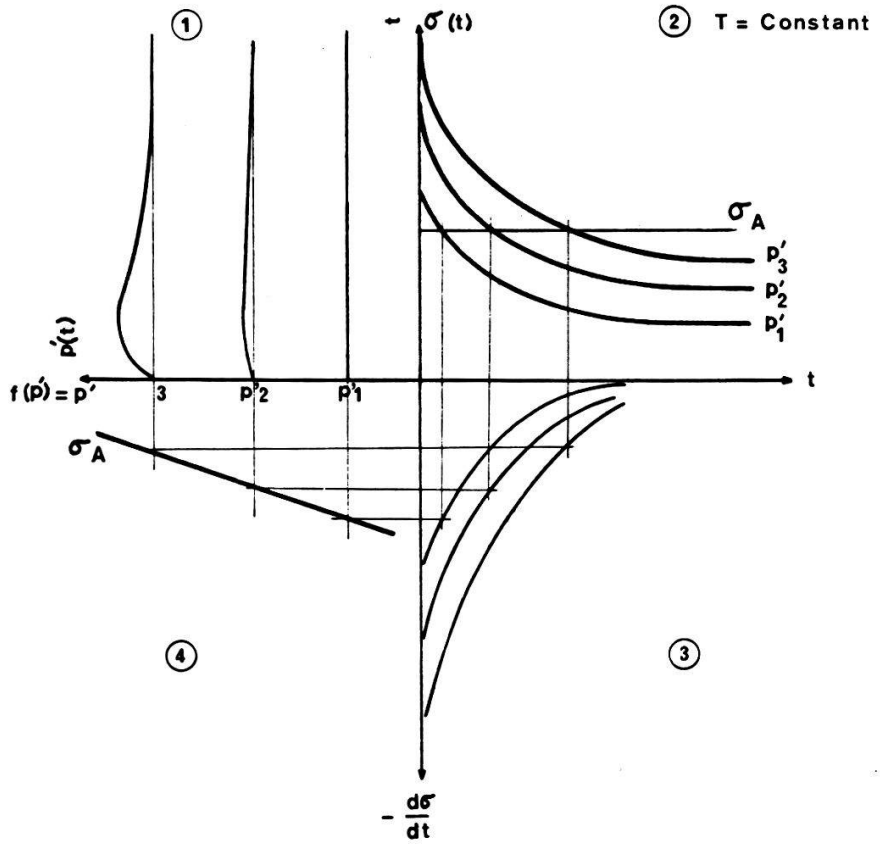

Figure 3
Procedure for the treatment of isothermal desorption data. ① Family of isothermal desorption curves $p'_{0j} - p'(t)$ for different equilibrium pressures p_{0j}; ② resulting surface population curves as a function of time ($\sigma(t)$); ③ resulting surface depopulation rate curves $d\sigma/dt$ as a function of time; ④ resulting dependence of $d\sigma/dt$ as a function of p'_{0j} ($d\sigma/dt = k_D h(\sigma) - k_A p'_{0j} g(\sigma)$).

representing in this case the decrease of surface population, is negative, because the desorption flux is greater than the readsorption flux. This check confirms the self-consistency of the whole procedure.

6. Conclusion

It is shown that a set of isothermal adsorption measurements on 'fresh' surfaces resulting from abrasion in UHV is in principle sufficient to give the controlling parameters of both adsorption and desorption reactions, provided a convenient and realistic model for their interpretation is designed in such a way as to account for both adsorption and desorption fluxes.

The combined use of abrasion with the model may constitute a new, easy and reliable technique for ultraclean investigation of the gas/solid interface.

This is practically true, in the case of the interaction of H_2 with nickel [1].

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