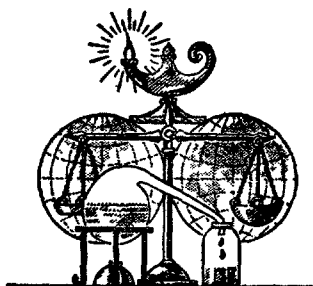# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY)

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INTRODUCTORY LECTURE

J. Th. G. Overbeek

van't Hoff Laboratory, University of Utrecht, Utrecht, The Netherlands

It is my task now to give a brief introduction to this Symposium and perhaps to announce a few subjects that we might want to emphasize in the discussions. The first idea for this Symposium was to obtain a survey of the different methods for surface area determination, to compare their results, and, if possible, to formulate recommendations for methods of measurement or calculation, that could be internationally accepted.

I do not need to stress that area or specific area ($=$ area per unit mass) is an *important* parameter of a finely divided solid (or liquid) phase. But *why* is it *difficult* to measure? The answer is: because it is not well defined. Determining the surface area of a solid is affected with the same difficulties as determining the surface area of *England*, or *Holland* or of the *Italian Dolomites*. On a small scale map the answer is simple, but it is not very accurate and it neglects the structure of the surface completely. So then we have to decide which part of the surface roughness is to be taken into account. Only those features that can be read from the map with elevation contours? Or the actual roughness of the rocks and soil? Or the roughness of the sandgrains and the individual pebbles? There is no unambiguous answer; only an arbitrary choice is possible.

The same is true for the surface area of a finely divided solid. And the choice will depend on the *use we are going to make* of the value of this surface area. Looking at the problem from this point of view, we want to know the complete geography of the surface, accurate to the kind of, and number of, the surface atoms, and including the way in which they are bound to the next lower layer. Such information would be good enough to explain all possible interactions with substances that can be adsorbed, move along the surface, react at the surface, or even move in the gas or liquid phase in the neighbourhood of the surface.

However, this detailed answer is as good as and about as useless as saying that all the properties of a glass of good wine are contained in the Schrödinger equation for its nuclei and electrons.

In the papers for this Symposium, these aspects are mostly not mentioned explicitly, but it will be well to keep them in mind in the discussions. Cases, where indeed this 'molecular' or 'atomic' way to look at the surface becomes preponderant are found when *crystallographic* data are used for surface area determination (assuming that the total surface consists of flat crystallographic surfaces) or also, when instead of asking how many molecules of nitrogen or of another adsorbate are packed on a certain area, one considers how many surface atoms of a given kind of molecule of a certain adsorbate is attached.

But in the main we will discuss surface area in these days from a somewhat simplified point of view, i.e., we form a kind of envelope through the centres

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of all the surface atoms, and consider the area of this envelope. In a great many cases we are not content to know the area of this envelope, but we want to know also, how it is folded in slits, pores, and other surface irregularities.

In discussing pores, most people will first think of cylindrical pores, but on second thoughts, these are rather improbable. Slits either between two parallel crystal faces, or perhaps wedge shaped slits are already more probable, and in the papers, the old ink-bottle image is used several times to describe a cavity with a narrow entrance. Remarkably enough the image of interstices between a mass of packed and possibly somewhat sintered particles, which might be applicable in several practical cases, is only rarely referred to.

Passing now to the papers presented at this Symposium, we find great emphasis on surface area determination by adsorption methods in different variants.

a_1. The methods used most frequently are based on the determination of the *monolayer capacity* of a given adsorbent by the BET method, by the t-method, which is based on it, or by adsorption from solution, using either simple molecules such as benzene or toluene, or large and complicated ones such as dyes. In order to convert the number of molecules in a complete monolayer to a surface area, one needs the area *per adsorbed molecule* and this requires a *calibration* based on the adsorption on a non-porous adsorbent, the surface area of which is known from other data. A very important question is then, whether the surface area per molecule is independent of the chemical nature of the adsorbent.

If the adsorbent is porous, application of the *Kelvin equation* leads in principle to the determination of the volume contained in pores of given sizes and so, with the aid of a pore model, to the distribution of the surface area amongst the pores. However, the method needs several refinements, one of these being the division of pores into *macropores* (too big for capillary condensation), intermediate pores or *mesopores* (typical for capillary condensation) and *micropores* (too small for application of the Kelvin equation).

a_2. Instead of using the adsorption isotherm at about the complete monolayer and higher coverages one may use the *low* (linear) *end of the adsorption isotherm* and when the Henry's law constant for the particular combination of adsorbent and adsorbate is known, derive a surface area from that part of the isotherm. Obviously, surface heterogeneity and the need of calibration with an adsorbent with known area are weak points of this otherwise attractive method.

a_3. For surfaces carrying an electric layer *negative adsorption* of the co-ions can be used to obtain a surface area. This method, which was first proposed by Schofield for clay surfaces, leads to an absolute value of the surface area without the need of a calibration, but it is not applicable to porous solids and in its present form it is not accurate for specific surface areas below a few m^2/g.

b. A completely different approach, leading without calibration to an absolute value for the surface area is based upon the determination of the *heat of immersion*. If the adsorbent is precoated with a sufficiently thick layer of molecules the liquid in which it is to be immersed, immersion results in

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the destruction of the surface areas containing a surface enthalpy per unit area equal to that of the free liquid and to the liberation of a corresponding amount of heat.

With presently available calorimetric techniques the method requires a non-porous solid with a specific surface area not less than 10 m²/g.

c. Another method or rather group of methods uses the *flow of a gas or liquid* through a plug or membrane to give information on its surface area. From the steady rate of flow, using the *Kozeny-Carman* method, a relation between porosity and surface area can be obtained. This method, however, does not take the area and porosity connected with blind pores into account. Moreover, a pore model and an estimate of the 'tortuosity' are needed.

Non-steady state methods, in particular the determination of adsorption— and desorption—time lags do give more information and, if judiciously applied, some information on the blind pores. From the adsorption isotherm, the total area can be obtained as in the methods considered under *a.*

d. In the case of expanding clays the surface area can be determined directly from x-*ray crystallographic* data, but this case is a rare exception.

Small angle x-ray scattering, on the other hand, allows the determination of the total surface area in the sample without any separate calibration. Moreover, information can be obtained on pore size or particle size distribution. A remarkable feature of this method is, that it also takes *closed pores* into account, which are inaccessible to all adsorption methods.

e. Finally, mention should be made of the use of the *electron microscope* or of the *ordinary microscope* for determining particle size distributions and surface areas of non-porous particles and of the important case of *carefully drawn glass fibres*, where length, mass, and density are sufficient to allow calculation of the area.

Summarizing, we find that there is quite a variety of methods available and, in favourable cases, more than one method may be applied to the same sample. The methods are of different reliability and of different accuracy; some are absolute, some need a calibration. It is one of the purposes of this Symposium to evaluate these methods critically and perhaps reach a conclusion as to which method or methods and which calibration parameters are to be recommended for particular purposes.