

# Measuring Particle Surface Area by Gas Sorption

## Why is surface area so important?

Because surface area is the means by which a solid interacts with its surroundings, be it gas, liquid or other solids. As particle size decreases, so does the surface area per unit volume (or mass). Furthermore, the generation of porosity, especially when due to small pores, can produce surface area far in excess of that produced by particle size reduction! On very coarse powders the specific surface area can be as low as a few square centimeters per gram, while on finer powders it might be a few square meters per gram. Porous materials having a significant volume of very small pores might exhibit a surface area larger than a football field - several thousand square meters per gram.

Specific surface area is often correlated with rates of dissolution and other rate-related phenomena such as catalyst activity, electrostatic properties of powders, light scattering, opacity, sintering properties, glazing, moisture retention, shelf-life and many other properties which can influence the processing and behavior of powders and porous solids.

Therefore, surface area measurement is probably the most widely used means to characterize porous materials. Since the surface area corresponds to the roughness of the particle exterior and its porous interior, gas sorption is the preferred technique. In contrast, particle sizing techniques, for example, calculate assumed area values based on smooth, non porous spheres!

So, for accurate surface area measurements, the temperature and pressure of an inert gas are adjusted to cause a single layer of gas molecules to be adsorbed over the entire surface of a solid, be it porous, no-porous or powdered. Pressure transducers or other sensors respond quantitatively to the amount of gas adsorbed. Using these data, and by means of a simple well-known calculation (**the B.E.T. equation**), it is easy to compute the surface area of a sample which is usually reported as the *specific surface area* (i.e. surface area per unit mass, usually  $m^2/g$ ).

## **BET**

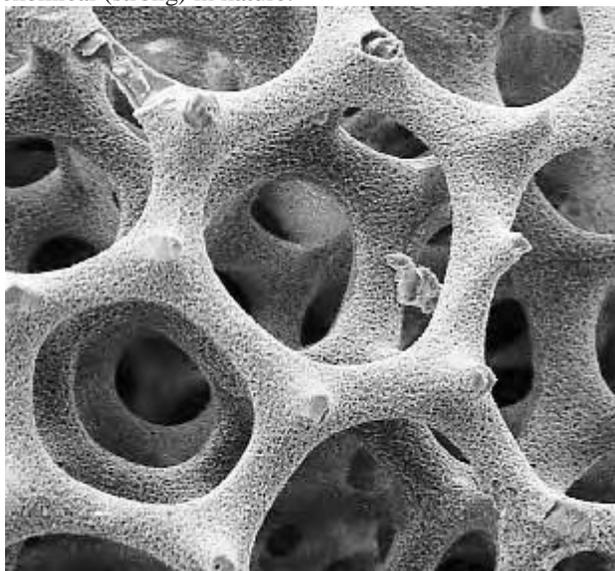
**The structure and reactivity of solid materials determine the manner in which their surfaces interact with gas molecules. Quantifying gas-solid interactions through the generation of gas sorption isotherms permits the routine evaluation of properties that control the performance of solids, such as surface area, size and shape of pores, chemically active sites, and many others.**

All matter is made up of atoms. In gases, atoms and molecules are free to move about in space. In contrast, atoms in solids are located in fixed positions by electrical forces of attraction among neighboring atoms. But the outermost (or *surface*) atoms in the solid have fewer neighbors than the atoms beneath them. To compensate for their electrical force imbalance, surface atoms seek to attract surrounding gas molecules. The tendency of all solid surfaces to attract surrounding gas molecules gives rise to a process called gas sorption. As illustrated by the ensuing examples, monitoring the gas sorption process provides a wealth of useful information about the characteristics of solids.

Before performing gas sorption experiments, solid surfaces must be freed from contaminants such as water and oils. Surface cleaning (degassing) is most often carried out by placing a sample of the solid in a glass cell and heating it under vacuum. Figure 1 illustrates how a solid

particle containing cracks and orifices (*pores*) of different sizes and shapes may look after its pretreatment.

Once clean, the sample is brought to a constant temperature by means of an external bath. Then, small amounts of a gas (the *adsorbate*) are admitted in steps into the evacuated sample chamber. Adsorbate molecules quickly find their way to the surface of every pore in the solid (the *adsorbent*). These molecules can either bounce off or stick to the surface. Gas molecules that stick to the surface are said to be *adsorbed*. The strength with which adsorbed molecules interact with the surface determines if the adsorption process is to be considered physical (weak) or chemical (strong) in nature.



Photomicrograph:  
Radiolaria

### Physical adsorption

(*physisorption*) is the most common type of adsorption. Physisorbed molecules are fairly free to move around the surface of the sample. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. Based on the well-known Brunauer, Emmett and Teller (BET) theory, one can estimate the number of molecules required to cover the adsorbent surface with a *monolayer* of adsorbed molecules,  $N_m$  (see Figure 2). Multiplying  $N_m$  by the cross-sectional area of an adsorbate molecule yields the sample's **surface area**.

Continued addition of gas molecules beyond monolayer formation leads to the gradual stacking of multiple layers (or multilayers) on top of each other. The formation of multilayers occurs in parallel to capillary condensation (see Figure 3). The latter process is adequately described by the Kelvin equation, which quantifies the proportionality between residual (or equilibrium) gas pressure and the size of capillaries capable of condensing gas within them. Computational methods such as the one by Barrett, Joyner and Halenda (BJH) allow the computation of pore sizes from equilibrium gas pressures. One can therefore generate experimental curves (or *isotherms*) linking adsorbed gas volumes with relative saturation pressures at equilibrium, and convert them to cumulative or differential **pore size distributions**.

As the equilibrium adsorbate pressures approach saturation, the pores become completely filled with adsorbate (see Figure 4). Knowing the density of the adsorbate, one can calculate the volume it occupies and, consequently, the **total pore volume** of the sample. If at this stage one reverses the adsorption process by withdrawing known amounts of gas from the system in steps, one can also generate *desorption* isotherms. Since adsorption and desorption mechanisms differ, adsorption and desorption isotherms rarely overlay each other. The resulting *hysteresis* leads to isotherm shapes that can be mechanically

related to those expected from particular **pore shapes**.

Some surfaces, especially catalysis, are sufficiently reactive to form chemical bonds with certain gases. In contrast to physisorption, **chemical adsorption** (*chemisorption*) involves the formation of strong chemical bonds between adsorbate molecules and specific surface locations known as **chemically active sites**.

Chemisorption is thus used primarily to count the number of surface active sites which are likely to promote chemical and catalytic reactions.

