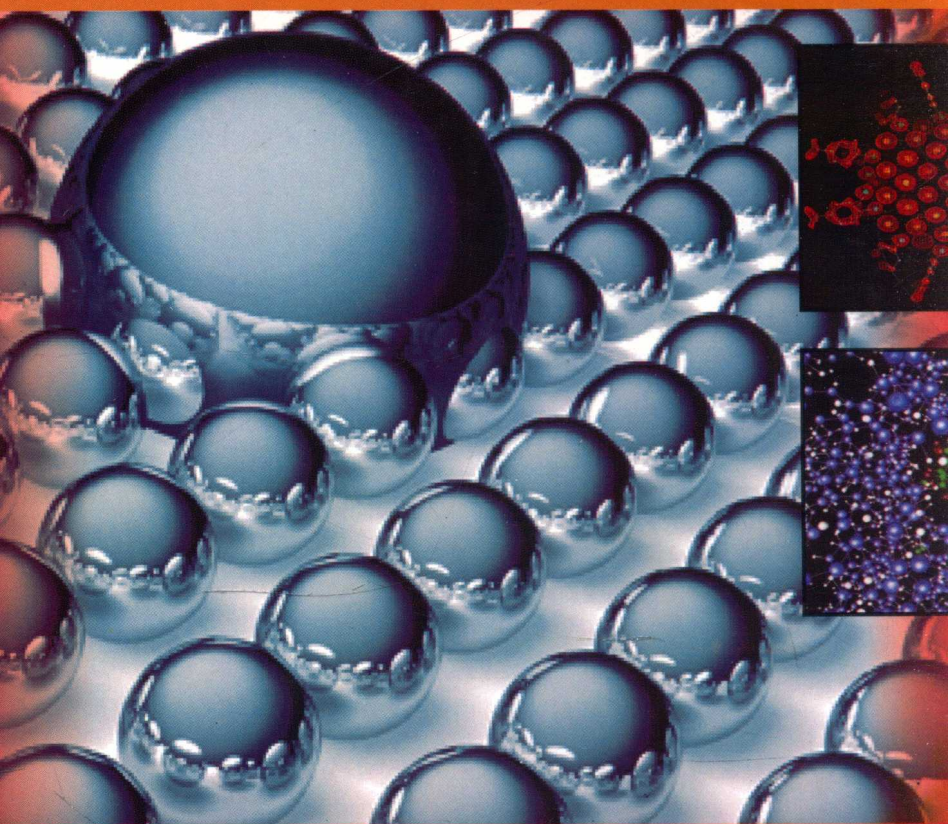


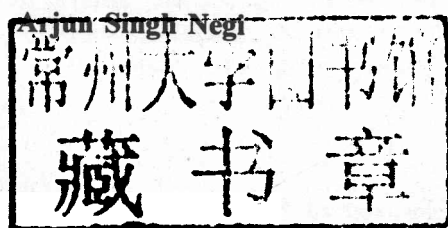
Elementary Surface Chemistry



Cyber Tech

Arjun Singh Negi

ELEMENTARY SURFACE CHEMISTRY



CYBER TECH PUBLICATIONS

4264/3, Ansari Road, Daryaganj, New Delhi-110002 (India)

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E-Mail: cyberpublicationsdelhi@yahoo.com

Website: www.cybertechpublications.com

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Arjun Singh Negi

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First Edition 2011

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Published by :

G.S. Rawat for Cyber Tech Publications

4264/3, Ansari Road, Daryaganj, New Delhi-110002 (India)

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**ELEMENTARY SURFACE
CHEMISTRY**

PREFACE

The "Elementary Surface Chemistry" book is provides all necessary information. While this was gratifying in one sense, at the same time there were many imitating features like typographical errors.

To familiarize the student about expected type of questions in the examinations, important summary and review questions have been provided at the end of each chapter. The subject matter has been presented in a simple and systematic manner. The present edition has many new features. This approach is adopted for some main reasons. Several sections in all these chapters have been rewritten and enlarged to make the text clear. So, the students written some querries and mistakes in this book.

The author shall be gratefully to the readers who point out errors and omissions which inspite of all care might have been there.

— Author

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1

Surface Chemistry

INTRODUCTION

The methods for measuring surface area, it may be well to define what is meant by the surface area of a porous solid. Quite clearly, a porous solid may be said to have two different types of areas. One of these is made up of the external, the geometric or the *outer surface area* of the porous particles. The other type is usually called the "*inner surface*" and is made up of surface of the walls of the capillaries, crevices and cracks in the porous catalyst particles.

Sometimes the ratio between the total surface area and the outer surface area needs to be stated. This ratio is usually known as the "*roughness factor*" of the solid. Such roughness factor may extend all the way from the value of unity for perfectly smooth solids upto values of several hundred or several thousands for very porous materials.

The specific surface area is defined as the surface area per unit mass (expressed as m^2/g). Various methods for the determination of surface area of solids are as follows:

1. *Harkins and Jura Method* : By assuming that the same type of equation is applicable to the adsorption of gases on solids that has been found applicable to correlating the surface spreading force of adsorbed films on liquids with the area occupied by adsorbed molecules. Harkins and Jura deduced that area of a solid can be obtained from the following equation:

$$\log \left(\frac{p}{p_0} \right) = B - \frac{A}{v^2}$$

where A and B are constants, and v is the value of the gas adsorbed at pressure p; p_0 is the liquefaction pressure of the gas. By plotting $\log p$

against $1/v^2$, the slope (S) of the curve obtained has been shown to be related to the area A of the surface by the equation

$$A = kS^{1/2} \quad \dots(1)$$

where A- is a universal constant which can be evaluated by an independent method.

In some very ingenious experiments, Harkins and Jura also provided an independent means of evaluating k by exposing a finely divided solid such as TiO_2 to a sufficient pressure of water vapour to form four or five statistical adsorbed layers, and then immersing in liquid water this sample got coated with several layers of adsorbed water. They were then able to obtain from the evolved heat of immersion a direct measure of the surface area of the powder without any assumption as to the molecular cross-section of the water molecule. They merely divided the heat of immersion by 118.5 ergs, the value for the normal surface energy per square cm of liquid water to obtain a value for the number of square cm of area in the sample. Using this surface area for the powder they were then able to evaluate the constant of equation (1). For other solids they could apply equation (1) by assuming that the constant k was independent of the type of surface. Proceeding in this way they obtained surface area values for six separate solids with their nitrogen adsorption isotherms and compared them with the areas that were obtained by plotting the adsorption data according, i.e., B.E.T. method.

2. *Benton and White Method* : Benton and White (1931) noticed a sharp break in the S-shaped isotherm for the adsorption of nitrogen at -191.5° on an iron catalyst at about 120 m.m. pressure. This apparently corresponds to a complete monolayer. It is evident that the product of the number of molecules in the monolayer and the molecular crosssection would give the surface area. This idea was further developed by Brauner who applied their B.E.T. equation to surface determinations. The isotherm may be put in the following form

$$\frac{x}{(1-x)V} = \frac{1}{V_m c} + \frac{(c-1)x}{V_m c}$$

where all letters are having the usual significance. The plot of the left hand side of this equation against x would give V_m and c. The plot is often linear at pressures x less than about 0.3, and this linear portion will, in general, extend to both sides of the pressure corresponding to a monolayer. In general, the monolayer

point would correspond to $x \approx 0.1$, when $c \approx 100$ and to $x \approx 0.5$ for $c = 1$.

It also becomes necessary to find the area covered by each adsorbed molecule so as to get the value for the surface area of the adsorbent. Emmett and Teller regarded that the area, A of each adsorbed molecule may be given by the relation

$$A = 4.866 \left(\frac{M}{4\sqrt{2} Nd} \right)^{2/3}$$

where M refers to the molecular weight of the gas, d the density of the liquefied or solidified adsorbate and N Avogadro's number. For argon and carbon dioxide at -183°C . the area has been found to be about 17 \AA^2 , for NK_3 at -36°C it has been found to be about 13 \AA^2 . For measurement of surface area, nitrogen is commonly used as the adsorbate at liquid nitrogen temperature (-196°C). Nitrogen is having a cross-sectional area 16.2 \AA^2 .

It is to be remembered that the areas obtained by the use of adsorbates other than nitrogen have been found to be different in many cases from those obtained by means of nitrogen. Thus, Harris and Emmett reported that for CS_2 the area might be only one-third to one-half as large as that calculated by the nitrogen adsorption method. In the same way, the areas obtained for butane and argon have been found to be different by a factor of 1.5 and 1.2. respectively. The reason for the discrepancies has been attributed to the larger molecules being screened out of some of the pores of the adsorbent, or to irregularities in packing of various molecules on the surface of the solid.

3. *B. E. T. Method* : Brunauer, Emmett and Teller derived an equation that has proved very useful in interpreting multilayer gas adsorption isotherms and in yielding information as to the surface area of solid catalysts. Their equation may be written in the form :

$$\frac{x}{V(1-x)} = \frac{1}{V_m c} + \frac{(c-1)x}{V_m c} \quad [\text{see Equation (45)}]$$

where x is the relative pressure of the adsorbate,

V is the volume of the gas adsorbed at x ,

V_m is the volume of the gas required to form a monolayer on the solid, and c is a constant which depends on temperature,

on the heat of the liquefaction of the adsorbate and the heat of adsorption in the first layer.

Compare with the general equation of a straight line

$$y = \text{intercept} + \text{slope } x.$$

It means that a straight line should be obtained if $\frac{x}{(1-x)V}$ is plotted against x . The slope of this line is

$$\text{slope} = \frac{(c-1)}{cV_m}, \quad \dots(2)$$

and intercept at y -axis is

$$\text{Intercept} = \frac{1}{cV_m} \quad \dots(3)$$

On adding Eqs. (1) and (2), we get

$$\text{Slope} + \text{Intercept} = \frac{(c-1)}{cV_m} + \frac{1}{cV_m} = \frac{c-1+1}{cV_m} = \frac{c}{cV_m}$$

$$\text{or } (\text{Slope} + \text{Intercept}) = \frac{1}{V_m}$$

$$V_m = \frac{1}{(\text{Slope} + \text{Intercept})} \quad \dots(4)$$

If one molecule of an adsorbent occupies an area of the total numbers of molecules present in a volume will occupy an area

$$S = \frac{\sigma V_m N}{22400} \quad \dots(5)$$

since the total number of molecules in volume V_m is $\frac{NV_m}{22400}$.

Calculate the volume of V_m from equation (4) and then substitute in equation (5) to get the value of S , the surface area of solid.

B.E.T. surface areas have been found to agree quite reasonably with values calculated from electron micrographs. The B. E. T. method provides a relatively easy way to evaluate the surface area.

The monolayer volume is usually found out by using the BET volumetric adsorption apparatus. The principle is simple. The pressure, volume and temperature of a quantity of adsorbate can be measured by the manometers M_1 and M_2 , the burette B , and thermometers T_1 and T_2 , respectively. The amount of gas present can be calculated. The gas is then brought in contact with the adsorbent sample (S) kept in the liquid

nitrogen bath C. As soon as equilibrium is attained after adsorption, the amount of gas left in the gas phase would be calculated.

The difference between the amounts of gas precepts initially and finally would give the absorbate 'lost' from the gas phase to the adsorbed phase. The accurate determination of the amount of the gas unadsorbed at equilibrium has been found to depend on a correct calibration of the 'dead space' i.e., the free space surrounding the adsorbent sample. This dead space volume is generally determined by using helium whose adsorption is negligible at liquid N₂ temperature. The true adsorption values are then corrected for the dead-space volumes.

4. *Point B Method* : In this method, the relative pressure p/p_0 is plotted against the volume of gas absorbed.

From the graph, the adsorbed volume necessary to yield a monolayer of gas on the surface is determined. This can be done by reading directly the amount, V_b , adsorbed corresponding to the first inflexion point (Point B). It is assumed that the adsorbate covers the solid as a monolayer at this point. Finally, the area per gm of the adsorbent is calculated by substitution of the relevant data in the equation.

$$S = \left(\frac{P' V_b}{RT_0} \right) NA \quad \dots(6)$$

where $P' = 1$ atmosphere

$T_0 = 273^\circ\text{K}$

$R =$ Gas constant

$A =$ Area occupied on the surface by a single molecule.

The main drawback of this method is that this method cannot be applied to all types of gas adsorbates and solids.

5. *From the Permeability to Fluids* : The volume of a fluid passing in unit time (dV/dt cm³/sec) through S cm³ of a porous plug of length L is approximately given by the Kozeny—Carman equation :

$$\frac{dV}{dt} = \frac{(p_1 - p_2) S}{\eta L S_0} \frac{\epsilon^3}{k(1 - \epsilon)^2} \quad \dots(7)$$

where $p_1 - p_2 =$ The driving pressure difference.

$\eta =$ The viscosity of the fluid.

$\epsilon =$ The relative volume of voids, and

$k = A$ numerical constant which is usually assumed to be equal to five (a pure number).

As all the quantities of equation (7) can be measured, one can measure S_0 (cm^{-1}) and from this, one can measure area of unit volume of the solid phase by applying the following equation :

$$S = \rho A_g$$

where ρ is the density of the solid.

Limitations of the Method : The various limitations are as follows :

- (i) The plug may be a felt of fibres, a compacted powder and so on, but should not contain any pores or voids with one entrance only; a pore is registered only if the fluid enters it from one and leaves it at the opposite end.
 - (ii) Surface roughness generally lowers the experimental values of dV/dt and this may cause an additional falsification of results.
 - (iii) Equation (7) was derived on the assumption that the gas-flow was laminar. If the pore diameter is small in comparison with the free path of the gas molecules (*i.e.*, when the pressures p_1 and p_2 are very small), then these molecules fly across the pores rather than roughly parallel to their axes and another term must be added to the right-hand side of the equation.
6. *From the Electrical Potential of the Adsorbed layer :* If a metal electrode like silver or platinum is placed in a solution like sulphuric acid with which it does not react, a potential is developed which may be measured by means of a sensitive galvanometer or vacuum tube volt meter that draws very little current. Now if a small amount of current is made to flow through the system (of the order of micro amperes per square centimetre), the potential rises to a new steady state value. The plot of potential versus time during the interval immediately after the start of current flow was nearly linear and of the form:

$$-E = kq + \text{constant}$$

where q denotes the amount of active material on the cathode surface or current time. The value of A : should vary from one system to the next only in proportion to the surface area and the ratio of k for two electrodes should give the ratio of the specific

surface areas. Joncich and Hackerman obtained areas for platinised platinum by applying the above method very close to those given by the BET gas adsorption method.

7. *From the Rate of Dissolution.* We know that a very thin layer of liquid in contact with a soluble solid very soon becomes saturated with the latter, *i.e.*, acquires the concentration C_0 equal to the solubility of the solid. After that, the rate of dissolution is determined by the rate of diffusion of the solute (which is proportional to the difference $C_0 - C$, if C is the concentration far from the solid), to the inverse thickness of the diffusion layer and to the area of the solid-liquid interface. Let m be the mass dissolved at time t . Then dm/dt is the rate of dissolution. If this derivative is measured for, say, a well polished cube of a solid material (sample 1) and for a powder of the same substance (sample 2), then $(dm/dt)_1 : (dm/dt)_2 = A_1 : A_2$, *i.e.*, the ratio of the rates of dissolution is equal to the ratio of the two areas. The geometrical area A_1 of a cube is readily obtained ; hence, also the geometrical area A_2 of the powder can be found.

The two most doubtful assumptions on which this method is based are:

- (i) The thickness of the diffusion layer is identical in the two samples, and
- (ii) the surface region of the powder is as perfect as its core.

If the above assumptions are ever satisfied, then A_g is the area of the boundary between the saturated film and the unsaturated solution so that it ought to be significantly smaller than the area derived from the gas adsorption measurements.

8. *From the Heat of Wetting :* In this method, 1 g of a powder, whose surface area is A_0 , is immersed in a liquid. Then, A_0 cm² of the gas-solid interface disappear and A_0 cm² of the liquid-solid interface form. If the two total surface energies per unit area are U_{23} and U_{13} , then the energy change in immersion process is $A_0 (U_{23} - U_{13})$ and the heat of wetting Q is said to be equal to this product (with a negative sign as exothermal heat is considered positive), *i.e.*,

$$-Q = A_0 (U_{23} - U_{13}) \quad \dots(8)$$

From the above equation, A_0 can be estimated. In an earlier work, a silica gel containing 3 – 6 per cent water was used.

9 *Radioactive Tracer Method* : In 1922, F. Paneth devised a method to determine the surface area of crystalline powders with the aid of radioactive atoms. By exchanging tracer atoms of lead with lead in the surface of a crystalline precipitate of lead sulphate, one can determine the number of lead ions on the surface of the crystals, and knowing the area occupied by one lead ion, one can find the total area of the powder. The area occupied by one ion of a substance on a surface can be calculated from the distances between ions in a crystal lattice of a solid. This quantity (ρ^2) may be obtained from the following equation :

$$\rho^2 = \frac{M}{aN_p}$$

where M is the mass of one molecule, a is the number of gram-atoms per mol of a solid, N is the Avogadro's number and p is the density of substance.

In this method, a powder of lead sulphate is agitated with a solution containing radioactive lead. Due to the exchange of ions, an exchange equilibrium sets in. Noting the change in the activity of the solution, one can establish the kinetics of the exchange reaction. Most of the exchange reactions follow the first order kinetics. Thus, the degree of exchange in the time t after the beginning of the exchange reaction can be found quite easily from the obvious relation:

$$x = \frac{a_0 - a_t}{a_0 - a_\infty}$$

where a_0 is the initial specific activity of the radioactive substance, a_t is the specific activity in time t after the beginning of the exchange reaction, and a_∞ is the specific activity of this substance after equilibrium sets in.

One can find the mass of the substance capable of participating in the exchange reaction with the aid of the following equation :

$$\frac{m_{\text{surface}}}{M_{\text{solution}}} = \frac{a_0 - a_\infty}{a_\infty} \quad \dots(9)$$

where surface is the mass of the substance on the surface of the solid capable of taking part in the exchange reaction and maximum is the mass of this substance in the solution. The mass of the substance in the solution can be found by ordinary chemical analysis. Hence it is easy to determine

from eq. (i) the number of ions on the surface (the quantity $m_{\text{surface}} = \frac{N_A}{A}$)

where A is the mass of one gram ion) and knowing the dimensions of ions, it is simple to find the total surface area of the crystals.

Importance of Surface Area

Surface area has been an important parameter in almost all physical and chemical processes which are involving powdered or porous solids. For example, catalysts used in dehydrogenation are having activities that are directly proportional to the total surface area. Measurements of surface area provide much information about the composition of the surface of a catalyst or an adsorbent. Knowledge of surface area has been found to be also very useful in following the changes in catalysts during use, sintering and impregnation.

The efficiency of adsorbents such as silica gel, activated alumina etc. in dehumidification of air and other gases and also in drying of liquids like oils and hydrocarbons, largely depends on their surface area. The extent of surface available in activated carbon has been a necessary information in large scale solvent recovery in many industries. Measurement of surface area has been thus the first step in any physical or chemical process using adsorbents or catalysts.

ALTERNATE DEFINITION OF SURFACE EXCESS

Suppose there are two bulk phases, α and β which are to be uniform upto an arbitrary dividing plane S . Let us restrict ourselves to plane surface so that C_1 and C_2 have been zero, and the condition of equilibrium does not impose any particular location for S .

If the unit area in cross-section, and further if the phases were uniform upto S , amount of the i^{th} component would be given by

$$xC_i^\alpha + (a - x) C_i^\beta \quad \dots(1)$$

Here the distance x and a have been relative to planes A and B located far enough from the surface region so that bulk phase properties prevail. The actual amount of component i present in the region between A and B would be given by

$$xC_i^\alpha + (a - x) C_i^\beta + \Gamma_i \quad \dots(2)$$

where Γ_i represents the surface excess per unit area. If it is positive, it implies an actual excess of the component is present and if negative, there is actually a surface deficiency. An alternative name for it has been *superficial density*.

For the case where phase β is gaseous. $C_i\beta$ may be neglected, and equations (1) and (2) become

$$xC_i^\alpha \text{ and } xC_i^\alpha + \Gamma_i$$

If a second arbitrary choice is now made for the dividing plane, namely, S' and distance x' , it must follow that

$$xC_i + \Gamma_i' = xC_i + \Gamma_i \quad \dots(3)$$

as the same total amount of the i^{th} component must be present between A and B regardless of how the dividing surface gets located. One then has

$$(\Gamma_i' - \Gamma_i) C_i = x - x'$$

so that

$$(\Gamma_i - \Gamma_1)/C_1 = (\Gamma_2' - \Gamma_2)/C_2 = \dots$$

or, in general

$$(\Gamma_i' - \Gamma_i)/N_i = (\Gamma_j' - \Gamma_j)/N_j \quad \dots(4)$$

where N represents mole fraction or

$$\Gamma_i N_i - \Gamma_j N_j = T_i N_i - T_j N_j \quad \dots(5)$$

As S and S' are purely arbitrary in location, equation (5) would be true only if each side separately equals a constant

$$\Gamma_i N_i - \Gamma_j N_j = \text{constant.}$$

From equation (11) Art 16.13 it is apparent that if an increase in the concentration of a solute lowers the surface tension, Γ will be positive, whereas if an increase in the concentration of a solute increases the surface tension, Γ would be negative. The former and latter phenomena are termed as positive and negative adsorption, respectively.

Inorganic salts when dissolved in water give rise to negative adsorption, while the dissolution of organic solutes gives rise to positive adsorption.

A detailed picture demonstrating how concentrations might vary across a liquid-vapour interface is depicted. The dividing line is drawn so that the two areas shaded i full strokes are equal, and the surface excess of the solvent would be zero. The area shaded with dashed strokes which is lying to the right of the dividing surface, minus the smaller similarly shaded area to the left of the dividing surface, would correspond in this case to positive surface excess of solute.