



# CATALYSIS

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## Principles and Applications

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**Narosa Publishing House**

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**NAROSA PUBLISHING HOUSE**

22 Daryaganj, Delhi Medical Association Road, New Delhi 110 002  
35-36 Grems Road, Thousand Lights, Chennai 600 006  
306 Shiv Centre, D.B.C. Sector 17, K.U. Bazar P.O., Navi Mumbai 400 705  
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ISBN 81-7319-375-4

Published by N.K. Mehra for Narosa Publishing House, 22 Daryaganj,  
Delhi Medical Association Road, New Delhi 110 002 and printed at  
Replika Press Pvt. Ltd., Delhi 110 040 (India).

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# Foreword

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The idea of conducting an orientation programme for research scholars is not only novel, but also timely. I understand from the feedback received from the participants of the first orientation programme conducted at the Department of Chemistry, Indian Institute of Technology, Madras during December 20 to January 4, 2000 that the participants were fully satisfied with the course and desired the repetition of similar courses in future years. The organizers of this have come up with the idea of bringing out in printed form, the material covered in this course and the results in this compilation. This volume contains chapters combining fundamentals, synthesis, characterization and applications of catalysis. Editors have taken particular care to include some aspects of homogeneous catalysis as well as basis of enzyme catalysis. They have attempted to arrange the various aspects in a logical fashion, but as a book with contributions from different persons, each chapter has its own style. In this sense, each of these chapters can be considered as a stand-alone unit and can be accessed and assimilated independently.

Bringing various aspects of catalysis in a single volume, especially covering the various techniques used in the elucidation of catalytic processes is a very difficult task and the editors have tried their best to achieve this end. This compiled volume will be certainly useful for anyone who wants to start a career in catalysis. The practicing catalyst chemists and technologists will also find something useful for their purpose. I hope this volume will receive the attention it deserves.

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## Preface

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An orientation programme in catalysis was organized for the benefit of research scholars at the Department of Chemistry, Indian Institute of Technology, Madras during December 20, 1999 to January 4, 2000. This course, conducted for the first time in India, was sponsored by the Department of Science and Technology, Government of India and was intended to motivate young students to undertake advanced research in catalysis and to impart the correct research methodology, reasoning and analysis. The orientation programme was well received by the students drawn from various research organizations, universities and other academic institutions spread all over India. The material covered in this course was intended to encompass the entire gamut of catalysis including both fundamental and applied aspects. All the participants expressed the desire that the material taught to them should be brought out in the form of a book so that it can serve as a source material for other students in catalysis. Besides, the course organizers also realized that such a book could also be useful as a template for future courses. Motivated by the enthusiasm shown by the participants and the lecturers, the editors have made a compilation of much of the material presented in the lectures in the form of this book. The authors of various chapters are specialists in the area of catalysis and come from reputed academic institutions, national laboratories and industrial R&D laboratories. Though, however much the editors desired to have all the lectures delivered in the course to be included in this volume, it has not been possible as some of our colleagues could not, for various reasons, provide with acceptable manuscripts for inclusion in this book. The editors thus regretfully realize that some topics, which were excellently presented in the course, do not find a place in this book. All the same, the material presented does cover a large area of catalysis and we believe that it will be immensely useful to graduate students and researchers in the field of catalysis. The material has been logically arranged to make the understanding of the subject easy and should act as a primer for the subject.

The editors wish to place on record their deep sense of appreciation to the Department of Science and Technology, Government of India for both funding the orientation programme and making a financial grant for bringing out this volume.

The editors thank all the contributors to this publication for helping us realize an objective, which would have forever remained in a conceptual stage without their support.

The editors thank Dr. P. Ratnasamy, Director, National Chemical Laboratory, Pune for kindly agreeing to write the 'Foreword' to this volume.

Every endeavour, more so a publication of this type, can be improved only with the help from the readers in the form of generous comments and suggestions.

B. VISWANATHAN  
S. SIVASANKER  
A.V. RAMASWAMY

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# 1. Physical Adsorption

B. Viswanathan

## 1. General Introduction

Since the coordination sphere of the atoms at the surface is not saturated, they exert residual forces, which can be utilized for bonding with incoming gas molecules. When a surface is in equilibrium with a gas, one finds, an increased concentration of gas molecules in the immediate vicinity of the surface than in the bulk gas phase. This preferential accumulation of gas molecules at the surface is called adsorption. This type of accumulation takes place normally regardless of the nature of the gas or the surface, though the extent of adsorption and the degree of interaction and so activation may vary widely from system to system. In a heterogeneous reactions catalyzed by solids, at least one of the reactants must be attached in some way for a significant period of time to the surface of the solid catalyst. This can be achieved through the phenomenon of adsorption.

Since the phenomenon of adsorption is thermodynamically a spontaneous process, it should be accompanied by a decrease in the free energy the system. When the gas molecules is adsorbed from the gas phase, it loses certain degree of freedom (one or more degrees of translational and rotational motion) and hence, the process is attended with a decrease in entropy, or  $\Delta S$  is negative. It is therefore, clear from the thermodynamic relation,

$$\Delta G = \Delta H - T\Delta S$$

that the adsorption is exothermic.

### 1.1 Physical Adsorption and Chemisorption

All known adsorption processes can broadly be divided into two types, physical adsorption and chemisorption according to the forces involved in the binding at the surface. Physical adsorption results from intermolecular forces, which normally arise from the interaction of permanent dipoles, induced dipoles and quadruples and hence are akin to the condensation of vapor to form a liquid. For this reason physical adsorption is also known as van der Waals adsorption. On the other hand, chemisorption involved rearrangement of the electrons of the interacting gas (adsorbate) and the solid (adsorbent) resulting in the formation of chemical bonds. Since chemisorption can, for all practical purposes, be regarded as a chemical reaction, it is essentially restricted to the surface of adsorbent and so results in only a layer of molecule thick on the surface. Our concept of chemisorption is closely linked to our ideas of what constitutes a chemical bond.

Usually the distinction between chemisorption and physisorption is not clear-cut. Empirically it is often possible to distinguish between the two types, but as is true of most classifications there are situations where the distinction is so ill-defined that one has to use several criteria to decide the group to which the adsorption belongs. These criteria are listed below.

#### *Criterion 1a: Magnitude of heat of adsorption*

The heat of adsorption is of the same order of magnitude as the heat of liquefaction of the adsorbate

and is rarely more than twice or thrice as large. In physical adsorption normally the heat liberated per mole of gas adsorbed is of the order of 8–25 kJ/mol though occasionally values as large as 85 kJ/mol have been reported. During chemisorption much larger values of heat of adsorption are encountered and they are of the same order of magnitude as the heat liberated in the corresponding bulk chemical reaction. For example, the heat of chemisorption of oxygen on metals is of the order of 400 kJ/mol. Generally the heat of chemisorption is rarely less than 85 kJ/mol, but values as low as that associated with physical adsorption are also known for some chemisorption processes.

#### ***Criterion 1b: Variation of heat of adsorption with coverage***

The heat of adsorption can vary with surface coverage mainly due to the inherent heterogeneity of the surface as well as due to lateral interaction effect. All the atoms on the surface are not in identical environment and so the surface is heterogeneous. These effects are particularly marked for chemisorption process. The lateral interaction forces being invariably repulsive, can cumulatively contribute to a decrease in the heat of adsorption with coverage just as inherent heterogeneity of the surface does.

#### ***Criterion 2: Specificity***

Since physical adsorption is akin to condensation, it will occur with any system of gas and solid provided that the conditions of temperature and pressure are suitable. On the other hand, chemisorption is highly specific, and will take place only when the gas is capable of forming a chemical bond with the surface atoms.

#### ***Criterion 3: Reversibility***

Physically adsorbed gas can be removed at the same temperature at which adsorption takes place by decrease of pressure, though the process may be slow. The slowness would be due to diffusion effect. The removal of a chemisorbed layer, however, required much more severe conditions like high temperatures or use of particle beams to displace the species from the surface.

#### ***Criterion 4: Extent of adsorption***

Under appropriate conditions of temperature and pressure, physical adsorption can proceed to multi-molecular layers while in contrast, chemisorption ceases once a mono-molecular layer is formed. It must be noted however, that subsequent physical adsorption on chemisorbed layer is possible.

#### ***Criterion 5: Pressure dependence***

Since physical adsorption is akin to the condensation process, it takes place to an appreciable extent only at pressures and temperatures close to those required for liquefaction. If  $p$  is the equilibrium pressure of the adsorbed film and  $p_0$  is the vapor pressure the bulk liquid at the temperature of adsorption, then it is generally observed that adsorption is not significant at values of  $p/p_0$  of the order of 0.01. This criterion may not be strictly applicable for adsorbents with very fine pores. Chemisorption process, on the other hand, proceeds at much lower pressures and at much higher temperatures.

#### ***Criterion 6: Rate of adsorption***

Physical adsorption simulating liquefaction requires no activation and can occur very rapidly. On the other hand, chemisorption like most chemical processes requires activation and hence, takes place rather slowly. The application of this criterion is subject to many complications.

(a) With highly porous or finely powdered adsorbents the passage of gas into adsorbent mass is often slow particularly at low pressures.

(b) Precise measurements of rate of adsorption may be hampered by the establishment of pseudo-equilibrium, that is the outer sides of the adsorbent are covered thickly with the adsorbate and the subsequent re-adsorption of the adsorbed film to give rise to a uniform coverage may be a slow process. Thus physical absorption can also appear to be a slow process.

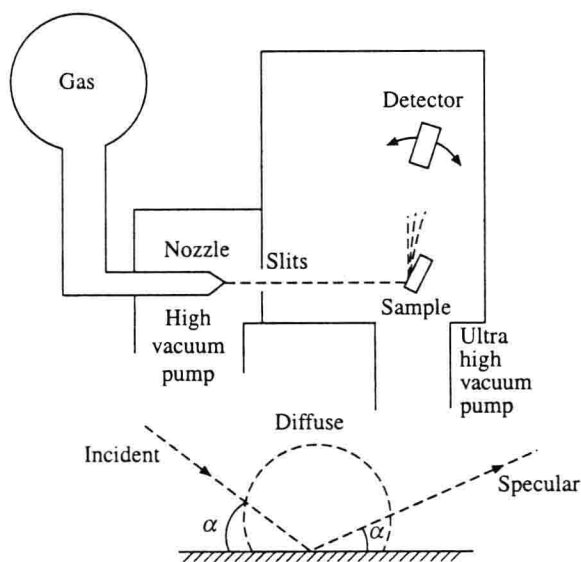
#### **Criterion 7: Rate of desorption**

The activation energy for desorption from physically adsorbed layer is rarely greater than a few kJ/mole, whereas the activation energy for desorption from chemisorbed layers is generally greater than 85 kJ/mol, the value being almost invariably greater than or equal to the heat of chemisorption.

## **2. Some Quantitative Aspects of Adsorption**

When a molecule with a certain kinetic energy strike a surface then its fate can be one of the following: (a) it can be reflected back without any energy changes; (b) it can penetrate into the solid and result in absorption, which is usually an endothermic process; (c) it can hinge on the surface for a period of time  $\tau$ , the mean residence time of molecules on the surface. In the last case the gas molecule exchanges some energy with the solid and the process as we have already seen, is usually exothermic (the concept of endothermic chemisorption as proposed by deBoer will involve prior dissociation of the adsorbed molecules).

The validity of the statement that the gas molecule striking the surface exchanges energy with the solid surface can be easily demonstrated with molecular beam experiments, (Refer to Fig. 1). The energy analysis of gas molecules in the secular as well as of non-secular directions will give information on the extent of energy exchange at the surface. Under these circumstances, the number of molecules which will be concentrated or adsorbed on the surface will depend on the number of molecules which strike the surface and on the duration of their stay. If  $n$  molecules strike unit area ( $1 \text{ cm}^2$ ) of a surface per unit time (1 second) and remain there for an average time  $\tau$  seconds, then the number of molecules



**Fig. 1.** Typical experimental setup to show that the molecules striking the surface exchanges energy.

which one will find at any instant on  $1 \text{ cm}^2$  of the surface, i.e. the number of molecules adsorbed per  $\text{cm}^2$  of the surface is given by

$$\sigma = \eta\tau \text{ molecules per unit area} \quad (1)$$

Both the parameters  $\eta$  and  $\tau$  are of great importance for the phenomenon of adsorption and hence require consideration.

The number of collisions,  $n$  is the number of molecules striking each  $\text{cm}^2$  of the surface per unit time ( $\text{sec}^{-1}$ ) and can be derived from the kinetic theory of gases as

$$n = \frac{N_p}{(2\pi MRT)^{1/2}} \quad (2)$$

where  $p$  is the pressure in dynes  $\text{cm}^{-2}$

$R$  = the gas constant =  $8.31 \times 10^7 \text{ erg. K}^{-1} \text{ mole}^{-1}$

$M$  = Molecular weight of the adsorbate

$N$  = Avogadro number =  $6.023 \times 10^{23} \text{ molecule g}^{-1} \text{ mole}^{-1}$

$T$  = Temperature (K)

substituting the constants in Equation 2, one obtains

$$n = 2.62 \times 10^{19} \frac{P}{(MT)^{1/2}} \quad (3)$$

if one has to express  $p$  in terms of mmHg, the expression for  $n$  becomes

$$n = 3.52 \times 10^{22} \frac{P}{(MT)^{1/2}} \quad (4)$$

Typical values for three common gases  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{O}_2$  at room temperature and 760 mm Hg are  $11.0 \times 10^{23}$ ,  $2.94 \times 10^{23}$  and  $2.75 \times 10^{23} \text{ molecules cm}^2 \text{ sec}^{-1}$ , respectively.

One notices that nearly 2 moles of hydrogen gas collide with each  $\text{cm}^2$  of the surface every second at atmospheric pressure. To provide an idea of the value of  $n$  in Equation 1 in molecular terms, some gas parameters as a function of pressure are assembled in Table 1. In this table the value of the mean free path  $L$  is roughly given by the relation.

**Table 1. Some gas parameters as a function of pressure**

	Pressure of gas		
	1 atm	1 $\mu$	$10^{-5} \mu$
Mean Free Path, $L$	$10^{-5} \text{ cm}$	7 cm	7 km
Average number of collision per molecules ( $\text{Sec}^{-1}$ )	$5 \times 10^9$	$6.5 \times 10^3$	$6.7 \times 10^{-2}$ (One per fifteen sec)
Number of molecules per $\text{cm}^3$	$25 \times 10^{18}$	$33 \times 10^{12}$	$33 \times 10^7$
Number of molecules striking a $\text{cm}^2$ of a surface per second ( $n$ )	$\sim 3 \times 10^{23}$	$\sim 3.5 \times 10^{17}$	$\sim 3.5 \times 10^{12}$
Time to cover (seconds) $1 \text{ cm}^3 (10 \text{ \AA}^2/\text{molecules})$	$3 \times 10^9$	$3 \times 10^{-3}$	$3 \times 10^2$

$$L = 10^{-5} \times \frac{T}{273} \times \frac{760}{p} \quad \text{or} \quad L = 2.784 \times 10^{-5} T/p \text{ cm} \quad (5)$$

where  $T$  is the temperature in Kelvin and  $p$  the pressure in mm Hg.

#### The time $\tau$

As stated earlier there are two possible things that can happen to a molecule striking a surface, it can either be influenced by the forces at the surface or it can rebound and return immediately to the gas phase. If it comes under the influence of the surface forces it may either remain on the surface for a short time and then return to the gas phase, or may stay there more or less permanently.

When the case of a molecule striking the surface and rebounding instantaneously to the gas phase is compared with that of a molecule returning after a brief period of stay on the surface, one notices very important differences concerning the direction in which the molecules leave the surface. In the case of the rebounding molecule which returns to the gas phase instantaneously, the direction in which it is reflected from the surface is related to the direction of incidence as in the reflection of light. If, however, the molecule remains on the surface for a short time before returning to the gas phase, there is no such relation and hence, no preferred orientation in any particular direction. The molecules in this case are scattered in all directions from the surface. This is one way to determine whether or not a molecule remains on the surface for a finite time. Experimentally, however, a difficulty may arise on account of the unevenness of the surface. If the surface is rough, even elastically reflected molecules will be scattered in all directions. Therefore, in order to find out experimentally whether it is genuine case of adsorption, scattering surface should be perfectly smooth or even.

In the case of the reflection of light, it is known that to avoid scattering, the unevenness of the surface must be such that the projection of the average height of the incident beam must be less than the wavelength of the light used. If  $h$  is the average height of the roughness on the surface and  $\theta$  the angle of incidence of the light of wavelength  $\lambda$ , then the condition for reflection is  $h \cos \theta < \lambda$ .

Extending the same condition for reflection of molecules striking a surface, let us consider  $\lambda$  as the wavelength of the material wave corresponding to the molecules. This is given by the relation  $\lambda = h/m\mu$ , where  $h$  is the Planck's constant,  $m$  is mass of the gas molecules and  $\mu$  is the average velocity of the molecules ( $\lambda \approx 10^{-8}$  cm for beams of light molecules, the wavelength of red light  $\approx 7 \times 10^{-5}$  cm) one can see that the condition of evenness required for reflection of molecular beams is about 100 times more exacting than that for reflection of light.

On such ideal smooth surface, it was found that with beams of light molecules such as hydrogen and helium the predominant phenomenon was reflection. With beams of heavier molecules like neon, argon and oxygen, there was very little or no reflection. For a beam of oxygen molecules ( $\lambda \approx 0.28 \times 10^{-8}$  cm) no reflection was found in the secular direction. It is therefore deduced that all the molecules hindered for some time on the surface before leaving the surface.

Experiments of the exchange of thermal energy between the impinging molecules and the surface also provide additional evidence for a time lag between impact of a molecule on the surface and its leaving the surface. These experiments also provide a measure of the extent of adsorption. When the molecules of a gas at a temperature  $T_1$  strike a solid surface at a temperature  $T_2$  there will be an exchange of heat if the time of contact is long enough. In the case of specular reflection, there will be hardly any exchange of energy. Complete exchange of heat will be found only when the impinging molecules stay on the surface for length of time which is large (say 100 times) compared with the period of vibration of surface atoms  $\sim 10^{-13}$  sec. For a smaller time of contact, there will be only a partial exchange of heat and the molecules returning from the surface will have a temperature  $T'_2$ ,

intermediate between  $T_1$  and  $T_2$ . To express the extent to which the impinging gas molecules "accommodated" their temperature to that of the surface, Knudsen defined an accommodation coefficient  $\alpha$  given by relation

$$\alpha = \frac{T'_2 - T_1}{T_2 - T_1} \quad (6)$$

The solid surface is assumed to undergo no change in temperature or it functions like a thermostat. The two extreme cases of no energy interchange  $T'_2 = T_1$  and complete equilibration  $T'_2 = T_2$  correspond to  $\alpha = 0$  and  $\alpha = 1$ . When the molecules fail to reach thermal equilibrium with the surface before leaving it ( $T_2 > T'_2 > T_1$ ),  $\alpha$  will be less than unity. The experimental method employed by Roberts for determining the accommodation coefficient is described below:

A fine metal filament of diameter about 0.07 mm and length about 18 cm is stretched in a cylindrical glass vessel, which is kept in a thermostat oil bath at the temperature  $T_1$ . The wire is maintained at a temperature,  $T_2$ , about  $20^\circ$  above  $T_1$  by passing a suitable electric current through it. A slow stream of purified (free of oxygen and other impurities) neon gas (which is practically non-absorbable) is passed through the vessel at a low pressure (0.1 mm Hg) such that the mean free path of the gas molecules is large compared with the diameter of the wire. Under these circumstances, the number of gas molecules  $n$  striking a square cm of the surface of the wire per second is given according to kinetic theory:

$$n = \frac{p}{(2\pi mkT_1)^{1/2}} \quad (7)$$

where  $p$  is the pressure of the gas in dynes  $\text{cm}^{-2}$ ,  $k$ , the Boltzmann constant and  $T_1$  the temperature of the gas molecules striking the surface of the wire. This temperature is taken as equal to that of oil bath  $T_1$ . The energy brought up thereby to unit area of the wire per second is

$$n \times 2kT_1 = \frac{p}{(2\pi mT_1)^{1/2}} \times 2kT_1 \quad (8)$$

Since  $2kT_1$  is the average energy per molecule of the gas at temperature  $T_1$ .

Under steady state, the number of molecules leaving unit area per second must be equal to the number striking it, but these molecules are supposed to be at the temperature  $T'_2 (> T_1)$ . And the energy carried away by these molecules is given by

$$n \times 2kT'_2 = \frac{p}{(2\pi mT_1)^{1/2}} \times 2kT'_2 \quad (9)$$

The net energy loss by conduction from the wire in ergs  $\text{cm}^{-2} \text{sec}^{-1}$  is given by

$$q_c = \frac{p}{(2\pi mkT_1)^{1/2}} \times 2k(T'_2 - T_1) \quad (10)$$

where  $k$  is in ergs  $K^{-1}$ .

Equation (10) can be rewritten using the Knudsen relation as

$$(T'_2 - T_1) = \alpha(T_2 - T_1) \quad (11)$$

$$q_c = \frac{p}{(2\pi mkT)^{1/2}} \times 2k\alpha(T_2 - T_1) \quad (12)$$

Substituting for  $m = M/N$  and  $k$  as  $1.38 \times 10^{-16}$  ergs  $K^{-1}$   $q_c$  is given by

$$q_c = 7.3 \times 10^3 \frac{\rho}{(MT_1)^{1/2}} \times \rho \alpha (T_2 - T_1) \text{ ergs cm}^{-2} \text{ sec}^{-1} \quad (13)$$

Neglecting heat losses due to radiation and conduction through the ends, which are usually small,  $q_c$  may be equated to the energy supplied to the wire to maintain it at the temperature  $T_2$ . Since all quantities other than  $\alpha$  is known in Equation (13),  $\alpha$  can be calculated. Roberts obtained  $\alpha$  value close to zero for pure neon gas with  $T_2$  values of 79 and 295 K. When a minute trace of hydrogen is admitted with neon, the accommodation coefficient rose immediately to about 0.18 at 295 K and to 0.28 at 79 K. Roberts also found that if the tungsten surface was previously covered with chemisorbed oxygen atoms, even inert gases like helium and neon (which gave  $\alpha \approx 0$  on the clean surface) gave appreciable  $\alpha$  values ( $\approx 0.3$  at 295 K). The values increased significantly as the temperature of the wire was lowered.

The results of determinations of accommodation coefficient show that while in certain cases (e.g. neon on clean tungsten)  $\alpha = 0$ , there are many cases where  $\alpha$  has higher values, sometimes approaching 1 (e.g. neon on oxygen covered tungsten surface; hydrogen on clean tungsten). In the later case,  $\alpha$  increases with decreasing temperature. As already explained  $\alpha > 0$  corresponds to situations where the impinging gas molecules stay on the surface long enough for energy transfer to occur before returning to the gas phase. The accommodation coefficient can also be considered to be a direct measure of the fraction of the surface covered.

Attempts have also been made to measure the time of residence  $\tau$  in a direct way. Hoist and Clausing reported in 1926 some interesting experiments in which a narrow beam of molecules was directed against a fast rotating disc. If the molecules really stayed for some time on this place before evaporating, they will have traveled a short distance with the rotating plate before being scattered. The molecules leaving the surface will naturally go helter and shelter in all directions, there being no preferred direction. If the molecules leaving the surface are, however, made to condense on a stationary plate which is strongly cooled, the center of the spot of condensed molecules, will not coincide with the opening through which the original beam of molecules emerged but will be displaced by a certain distance in the direction of rotation on the rotating plate. The extent of this displacement will depend on  $\tau$  as well as on the speed of the rotating plate. Since the evaporating molecules have an extra component of velocity due to the speed of the rotating disc, correction has to be applied to the measured displacement. It was, however, realized that the direct measurement of  $\tau$  by this procedure was rather difficult. All that could be established at that time was that cadmium vapor molecules impinging on glass surfaces at 200 K do have a finite time of residence though the actual value can be anywhere between  $10^{-6}$  and  $10^{-12}$  sec. In 1930, Clausing had worked out a more reliable indirect method for determining  $\tau$ . This method was based on the estimation of the velocity with which the gas molecules passed through narrow capillaries. When the pressure is sufficiently low so that mutual collisions are minimized the molecules collide only with the walls of the capillary and remain there for a time  $\tau$  before leaving surface. The average time taken by a molecule in order to pass through such a capillary of length  $l$  and diameter  $d$  is given by equation (14)

$$\bar{t} = (l^2/2d\bar{u}) + (l^2\tau/2d^2) \quad (14)$$

where  $\bar{u}$  is the mean velocity of the molecules. When  $\bar{t}$  is measured,  $\tau$  can be estimated by means of the following expression (15)

$$\tau = [2d^2/l^2][\bar{t} - (l^2/2d\bar{u})] = [(2d^2\bar{t}/l^2) - (d/\bar{u})] \quad (15)$$