Concepts in Catalysis

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1968
Academic Press London & New York

ACADEMIC PRESS INC. (LONDON) LTD
Berkeley Square House
Berkeley Square
London W.1

U.S. Edition published by

ACADEMIC PRESS INC.
111 Fifth Avenue
New York
New York 10003

Library of Congress Catalog Card Number: 68-17669

Printed in Great Britain by
Spottiswoode, Ballantyne and Company Limited
London and Colchester

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Chapter 1

Introduction

Fifty years ago Sir Hugh Taylor and I had the opportunity of writing *Catalysis in Theory and Practice*, in which we attempted to give an account of the catalytic phenomena known at the time. During the intervening years both the scientific inquiries as to the "modus operandi" of catalytic action and the technical developments in catalytic industrial processes have grown at an ever accelerating pace. This growth has been greatly stimulated by the utilization of new tools either chemical, such as the ortho–para hydrogen, deuterium and tritium reactions, labelling with radioisotopes and the development of knowledge of ligand structure in organometallic compounds, or physical, involving the methods of detection of free radicals and the properties of semiconductors, as well as the various magnetic, optical and electronic devices for examination of catalytic systems. On the industrial side the processes of ammonia synthesis and oxidation as well as the hydrogenation of unsaturated oils are now so firmly established as fundamental in world economy and the ever expanding range of chemicals provided by the petrochemical industry so important as to ensure that research on catalytic mechanisms will not be confined to academic laboratories.

The growth is revealed throughout the world in industrial plants, in Institutes devoted to the study of catalysis and to a truly frightening expansion of the literature on the subject. The compilation of a book on heterogeneous catalysis would consequently present a very formidable task. It is for personal reasons that I have ventured to put pen to paper in an attempt to portray some aspects of the subject which have impressed me. As an undergraduate and in my early graduate years at Cambridge, I was deeply influenced by Sir William Hardy and later by Irving Langmuir. A belated tribute to the memory of two lifelong friends might not be out of place in acknowledgment of my indebtedness to them. If any more formal dedication is required it is to those working in the laboratory at Cambridge who were sufficiently intrigued with the problems of heterogeneous catalysis to maintain their contributions to this subject when they went out to take their several parts in the life of the scientific community. These include R. M. Barrer, R. C. L. Bosworth, F. P. Bowden, D. D. Eley and A. and L. Farkas, E. F. G. Herington, C. Kemball, H. W. Melville, J. K. Roberts, H. Steiner, B. W. M. Trapnell, G. H. Twigg and A. F. H. Ward. As is clear from the title of this book, I have not attempted to write a comprehensive volume on heterogeneous catalysis but have drawn largely from the work of my colleagues and the material of my lectures to discuss some of the factors which may play a part in these surface chemical reactions. I pray forgiveness for many sins of omission and commission in the text.

In looking over the manuscript I note that several of the views expressed appear to be mutually exclusive. This may be due in part to a deceptive simplicity apparent in many reactions. The introduction of hydrogen isotopes and of the ortho–para reaction into catalytic reactions of the hydrocarbons has thrown a great deal of light on the mechanisms involved but has raised as many questions as it set out to solve. Again, there is a considerable latitude in the interpretation of experimental data in terms of mechanism. Preconceived views or choice of analogies may play a dominant part in one's opinion. As an example we note that data both recent and accurate on the adsorption isotherms of hydrogen on carbon have been interpreted both as an adsorption on fixed sites with lateral interaction and as a two-dimensional Van der Waals gaseous state. The classical example of a heterogeneous catalytic reaction, namely the hydrogenation of ethylene (a system which possibly has been studied more than any other), still provides an area for vigorous debate. In the field of catalysis the crucial experiment is often a will o' the wisp and eludes our grasp.

Fifty years ago, two contrasting views on the regulatory mechanisms were firmly held: that of Sabatier in the concept of the formation of intermediary chemical compounds and that of Faraday, revived by Bodenstein, in the theory of diffusive control. Langmuir's development of the idea of the orientated monolayer and the recognition of the distinction between physically adsorbed and chemisorbed species by H. S. Taylor in his work on activated adsorption greatly supported the chemical view and the conditions necessary for limitation by diffusive control in any given reaction were readily established.

During the intervening years, our knowledge concerning processes of condensation and evaporation has been greatly extended and we have witnessed the development of electronic concepts in the formulation of the band, the valence bond, the crystal field and the structural ligand theories, the last mentioned being an introduction to the prosthetic group in enzymes, to interpret the mechanism of the electron shift implicit in the chemical reaction. We are indebted to G. M. Schwab for formulating these mechanisms on metals and to Wagner, Garner and F. F. Vol'kenstein for its application to semiconductors. The transition from co-operative to individual catalytic units in a solid catalyst has likewise been proposed as a result of extensive work on semiconducting oxides and sulphides.

In spite of many careful experiments, our knowledge of the heats of adsorption especially for chemisorption leaves many questions unsolved. This is also the case with respect to the problem of surface mobility, an understanding of which is fundamental to any theory of mechanism in surface reactions. Concerning recent discussions on heterogeneous catalysis, there emerge from one's memory some remarks made by Eddington to the effect that progress is not measured by the problems which have been solved but by the questions one can ask. In the field of heterogeneous catalysis many old questions still remain unanswered.

Chapter 2

General Properties of Catalysts

Catalysis is the phenomenon in which one or more substances isothermally (and non-radioactively) augment the rate of a chemical reaction without appearing in the stoichiometric equation of the reaction. In heterogeneous catalysis the catalyst constitutes one or more phases which are distinct from those formed by reactants and products.

In cases where the rate is augmented with increase of concentration of one or more products or of the surface of one or more phases formed by products, the phenomenon is called autocatalysis. This definition of catalysis differs only in preciseness from that of Berzelius, who originated the term.

In dealing with reversible processes, e.g.

$$\mathrm{A+B \rightleftharpoons C+D},$$

the intrusion of a catalyst into the system provides an alternative path, but does not alter the equilibrium. Consequently, both forward and reverse reactions are catalysed to equal extents. It is thus important in investigations on catalytic activity to have prior knowledge of the conditions of equilibrium of the systems under investigation. This is especially the case when we are interested in the problem of yields in the conversion of reactants into products. The small yield of ammonia from nitrogen and hydrogen obtainable under ordinary pressures and high temperatures is a historically important case. In the above reaction with gaseous reactants the free energy relationships can be obtained from thermal data, making use of the Van't Hoff isochore and the Nernst heat theorem

$$\Delta G_0 = -RT \ln K_p = -RT \ln \frac{[\mathrm{A}]\,[\mathrm{B}]}{[\mathrm{C}]\,[\mathrm{D}]}$$

and

$$\ln K_p = -\frac{\Delta H_0}{RT} + \frac{\sum \nu C_p \ln T}{R} + \frac{\sum \nu_\beta}{R} + \sum \nu i$$

necessary specific heats and chemical constants being derived from experimental data.

Although the phenomenon of catalysis can intrude at the liquid–gas or liquid–liquid interface it is with solid surfaces that we are most concerned. Solid surfaces are more complex than liquid surfaces in that they usually present areas or points of non-uniformity whereas the latter are surfaces of equipotential. Many catalytic reactions are brought about by the presence of metals or simple compounds such as oxides or sulphides, and in many cases the admixture of relatively small quantities of another compound can produce a great enhancement of the catalytic activity. The use of such "promoted" catalysts is now general. Since catalytic reactions depend on the available surface, it is common practice to impregnate a carrier or support material with the catalyst and thus produce an extension of the surface. Such carriers may have other important properties: thus they can affect the mechanical strength, impose a restraint on the rate of recrystallization and grain growth or improve the packing characteristics, and, in addition, they may affect the life as well as exerting some promoter effects on the catalyst itself. The promoter effects may be due to epitactic alteration in the atomic spacing of the catalyst or to modification of the "valency" because of incorporation in the crystal field. Since the extension of the catalyst surface is of importance, factors such as porosity, i.e. the size and distribution of the pores and their stability, have to be taken into consideration. It is evident that limitations are to be expected, dependent both on the sizes of the molecules of reactants and products as well as on diffusion rates operative during reaction.

We can thus distinguish between the available surface, the true surface and the apparent surface, i.e. that determined by consideration of the external dimensions of the catalyst alone. The ratio of the available to the apparent surface, sometimes termed the specific surface, consequently depends on the nature of the reactants involved, and the relationship to the true surface (m^2 g^{-1}), in its turn, depends on the method adopted for its measurement.

It is customary to employ the Brunauer-Emmett-Teller (B.E.T.) method for the measurement of the specific surface, using either nitrogen or a rare gas. Although this gives some general concept as to the difference between catalysts prepared in different ways, owing to the complexity of the surface structure and the possibility that catalytic activity is limited to certain regions of the surface, the inferences drawn from B.E.T. data have to be used with caution. This is evident when supported catalysts are under consideration. A gas selectively adsorbed by the catalyst and not by the support should be chosen. For this purpose it is preferable to use either hydrogen or carbon monoxide; the former gas may introduce considerable errors by penetration and solution in the catalyst. Although the chemisorption of carbon monoxide introduces considerable selectivity, there is still some uncertainty, due to the fact that there are two forms of the chemisorbed gas: the linear form and the bidentate form, $\mathrm{CO_a}-$ and $\mathrm{CO_a}<$ respectively. There is a high probability that, when a monolayer is complete, only the former (yielding $1{\cdot}2 \times 10^{15}$ molecules cm^{-2}) is present. A strong case can be made for the use of oxygen at 80°K.

The use of radioactive and isotopic methods for the evaluation of the specific surface is becoming more frequent. Careful work on exchange methods of silver and the halogens, where the adsorption takes place by an exchange mechanism, e.g.

$$\mathrm{AgCl} + \mathrm{Cl}_2^* \rightarrow \mathrm{AgCl}_3^* \rightarrow \mathrm{AgCl}^* + \mathrm{Cl}_2,$$

shows that, although surface coverage is rapid and limited only by diffusion in the gaseous or liquid phase, this is followed by a slower process in which bulk exchange diffusion takes place following the usual Fick law which, for unit surface area, is

$$w = \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} = 2k\sqrt{\left(\frac{Dt}{\pi}\right)}$$

where D is the diffusion coefficient. Provided that the energy of activation for the diffusion rate is not too low, e.g. $E_D > 1{\cdot}0$ eV, the two processes can be experimentally differentiated from one another.

Another general method for determining the surface area of a catalyst without reference to the specific cross-sectional area of the adsorbate consists in measuring the heat of immersion of the solid in two stages, firstly in the vapour of a liquid up to the saturated vapour pressure and then the additional heat liberated on immersion of the vapour-saturated solid in the liquid. We obtain

$$\Delta H_{sl} = \Delta H_{sv} + \Delta H_{s\cdot l}$$

where ΔH_{sl} and ΔH_{sv} correspond to the heats of immersion in liquid and vapour respectively, and $\Delta H_{s\cdot l}$ is the energy change associated with bringing the wet solid and liquid or two liquid surfaces together. This is equal to $2U$ where U is defined by the equation

$$\gamma = U + T\frac{\partial\gamma}{\partial T}$$

γ being the free surface energy of the liquid covering the adsorbent.

Evidently, this method is not suitable for exact work because parts of "accessible" surfaces may fill up with liquid in the capillaries as the vapour pressure increases in accordance with the Kelvin equation and, in addition, even on the plane surfaces, as the vapour pressure p approaches p_0, more than a monolayer of vapour will be condensed, liberating heat.

As might be anticipated, since the surface of the solid catalyst alone is involved in the catalytic process, catalysts are extremely sensitive to the presence of impurities, which can find their way to the surface either from the surrounding gaseous or liquid phase, or by a process of diffusion from the interior of the catalyst or its support. Such impurities can be adsorbed on the surface and thus act as poisons.

In many cases poisons can be removed unchanged by desorption. Other means of removal are as a compound formed with the catalyst by suitable elevation of the temperature and by displacement by another gas or conversion into a more volatile product by chemical reaction, frequently with air or steam. If the quantity of poison in the reactants, or formed as a side reaction during reaction, remains constant, and the poison is a reversible one, the reaction rate may acquire a steady state after a period of induction. The rate under these conditions may bear no relationship to the true catalytic activity.

In experimental work with metallic catalysts, reactions can be studied with the catalyst in the form of a wire that can be electrically heated to any desired temperature. This method, due to Irving Langmuir, has a wide range of applicability. Equally important is that involving the evaporation of the catalyst and condensation as a film or mirror on the interior surface of a cooled container. Evaporation can be effected as originally employed by O. Beeck by means of a hot wire, or by electron bombardment of a small bead of the metal. Coprecipitation of a mixture of soluble salts of metal and carrier permit the preparation of active supported catalysts. Metals can also be deposited on carriers such as magnesia, magnesite or diatomite brick either directly or by ignition of salts deposited by evaporation from a solution; the most suitable salts are those that leave no appreciable residue except the metallic oxide. Oxalates, carbonates, formates or nitrates are customarily employed, the oxide being subsequently reduced by means of hydrogen.

Amongst the methods which have more limited application are the electrolytic deposition of the catalyst on a less active electrode, the deposition by cathodic sputtering or by condensation of the vapour from a vapour gun.

Highly porous metallic catalysts may be formed from alloys of nickel or cobalt with aluminium or silicon, the metallic skeleton derived by leaching out with caustic soda being a particularly robust and effective catalyst for hydrogenation reactions.

Colloidal solutions of catalytic metals are readily prepared by reduction in solution of the appropriate salts. Their high catalytic activity and many similarities to the biocatalysts, the enzymes, have maintained interest in these somewhat unstable and non-robust systems.

Surface Structure

Crystals grow with well-defined facets in which the lattice spacings are characteristic of the planes. If we regard the lattice energy of a crystal as comprising the sum of the interactions between one atom and its nearest neighbour and next nearest neighbours, each interaction of each type being identical, the energy of adsorption of the atom will evidently depend on its position in the crystal and on the crystal structure. If we denote the two interaction energies by u_1 and u_2, respectively, the energies of adsorption on the different facets of a body-centred cubic crystal will be $4u_1+u_2$ on the [100] plane, $2u_1+2u_2$ on the [110] plane and $4u_1+3u_2$ on the [111] plane. The heat of sublimation $(\Delta H_s+(RT/2))$ is $4u_1+3u_2$. Not only will the edges and corners of the crystallites differ in their free energies as well as the various planes but the spiral growth of crystals will, as Frank has shown, produce screw dislocations; consequently, steps and other surface imperfections (lines of dislocation, stacking faults and twins revealed by diffraction patterns and electron microscopic examination) as well as point defects, i.e. atomic vacancies, will be present. In addition, there will be a variable quantity of intercrystalline cement or amorphous metal. The heat of adsorption on a step is some twice and in a kink some three times that on the plane surface. Although it is possible that some reactions, e.g. the H_2–D_2, reaction, proceed on all the exposed surface of the catalyst, the experimental work available at present strongly suggests that, in general, catalytic activity is confined to limited areas of the catalytic surface.

Active Patches

The active patch hypothesis of H. S. Taylor and the necessity for *suitable atomic spacing of the substrate metallic atoms* insisted upon by Balandin each has its protagonists. In view of the crystalline nature of the metals, the concept of a Gaussian distribution of patches or assemblies of different free energies is unlikely and it is much more likely that a limited number only of such individual areas exists, namely the different crystal planes that may be present. Again, since the atomic spacings on different planes may differ, it is most likely that the catalytic activity may vary from plane to plane or even be confined to one plane On each of these planes there must exist lattice vacancies and dislocations. The extent of these in a metal can be determined by the rate of release of strain energy, and by changes in density, electric resistivity or hardness. In metals such as copper and nickel, changes in these properties take place within narrow temperature ranges. At lower temperatures (T_r), the atomic movement is sufficient to fill up the vacancies and at a higher temperature (T_d) recrystallization removes or diminishes the lattice defects.

The temperature range over which the lattice defects suffer diminution in number is affected by the number of defects present and the extent of the consequent lowering of the strain energy.

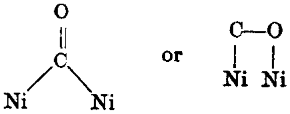
It has been claimed that the decomposition of benzene diazonium chloride, the dehydrogenation of ethyl alcohol on cold worked copper and a variety of catalytic actions on copper suffer relatively great diminutions in velocity when the catalysts are heated over the two ranges T_r and T_d.

In light of the facts that in annealing processes the area of any particular plane may well suffer a drastic reduction and that in the release of strain energy the interatomic distance changes the inference that the active centres for catalytic activity are confined to the lattice defects and dislocations is scarcely justified at present. It seems more reasonable to regard the crystal facet as uniformly active, although stronger adsorption and even some modified chemical activity at the dislocation need not be excluded.

It is worthy of comment that chemical reactivity and phase discontinuities are found to be related in many cases of chemical action. Ostwald and, later, Langmuir pointed out that in cases of dissociation, e.g. of $CaCO_3$, when equilibrium is established the dissociation of the $CaCO_3$ and its reformation from the resulting CaO must be confined to the common interface in order to satisfy the conditions imposed by the phase rule. Faraday was the first to observe the necessity for a discontinuity and its subsequent autocatalytic growth in the dehydration of salts with water of crystallization, and the reduction of various metallic oxides proceeds most rapidly at the metal–metal oxide interface.

Regional catalytic activity has been experimentally observed for the decomposition of ammonia on a monocrystal of copper where the [111] facet was found to be twelve times more active than the [100] plane. A similar selective action has been noted for the decomposition of formaldehyde on the same metal.

The decomposition of carbon monoxide proceeds most rapidly on the [111] planes of both copper and nickel. More evidence of an indirect kind is available to suggest that certain crystal facets only possess either all or a maximum of catalytic activity. With a model surface of uniform lattice the availability of the surface for adsorption evidently depends on the lattice spacing as well as the dimensional relationship to the adsorbate. In the case of hydrogen atoms on a metallic surface the whole of the surface can be covered, but a mercury atom (where Hg—Hg is 3·05 Å), if placed on a lattice point of the catalytic metals where, on the [110] plane, Ni—Ni is 2·48 Å, Pt—Pt is 2·78 Å, Rh—Rh is 2·69 Å, Ru—Ru is 2·65 Å and W—W is 2·74 Å, will overlap three or four of the nearest substrate neighbours, the number depending on the lattice plane considered. These partly shielded atoms may be capable of accommodating hydrogen atoms or some other adsorbate. This factor of surface availability becomes more clearly defined when multipoint contact is considered. The simplest example of this involves two-point attachment of three different types; two of these, in which two atoms of the substrate are involved for each molecule adsorbed, may be exemplified by the adsorption of carbon monoxide on nickel as



and the other by the adsorption of an olefin on the same metal. An olefin such as ethylene is bonded to the surface either by π- or 2σ-bonding, the two carbon atoms being bonded to two neighbouring nickel atoms. In a face-centred cubic nickel crystal the distance of closest packing is 2·48 Å and the size of the unit cell 3·50 Å. Taking the Ni—C and the C—C distance bond lengths as 1·82 and 1·53 Å respectively, it is not possible to fit ethylene on to the 3·50 Å spaced nickel atoms but only on the [110] 2·48 Å spaced plane. If a tetrahedral angle between carbon and metal atom is assumed, the metal spacing would be some 2·73 Å suggesting that rhenium (2·74 Å) and rhodium (2·69 Å) would be the most active metals; if the lattice expands from palladium, platinum to iron, the activity falls and, if the lattice contracts to nickel and tantalum, the activity is likewise reduced. In accordance with Balandin's views, the hydrogenation of benzene on alloys of iron and nickel takes place only on face-centred cubic structures, where it is possible to get adsorption of the benzene ring as a π-adsorption complex on a hexagonal lattice. Ernest and Skau extended this work to copper, nickel, silver and palladium alloys. Investigating the silver–palladium system, the palladium, being face centred and within the Balandin limits, was active but the silver, which is also face centred but outside the Balandin limits, was inactive. There is a decrease in activity in the alloys as the proportion of silver is increased. This decreased inactivity in hydrogenation may be in part, as we shall have occasion to note, a mere reflection of filling up the *d*-band vacancies, the catalytic metals themselves possessing *d*-band vacancies. Superimposed on this is the necessity for the presence of a hexagonal array of catalytic metallic atoms: thus it has been claimed that small quantities of rhenium on a carbon carrier are more effective than larger quantities deposited on alumina, where the cubic crystalline γ-Al_2O_3 is less effective as a support than α-Al_2O_3.

From models it can be shown that ethylene will almost cover the whole surface but substituted ethylenes, increasing from isobutene to trimethylene, cannot be accommodated in close packing and they leave isolated metal atoms accessible to the adsorption of hydrogen, as revealed by the ortho–para reaction.

The third type of reaction involving two-point attachment is to be found in the adsorption of diatomic gases, where dissociation is involved. Since adsorption takes place in pairs when the lattice has been filled there will remain, if the chemisorbed atoms are not mobile, some 8·6 % of the surface bare in the form of isolated sites. Above these sites molecules can be held more tenaciously than above the covered surface. We shall note that several varieties of adsorbed species may co-exist even for the elementary gases.

Physical Adsorption

Physical adsorption or van der Waals adsorption, in contrast to chemisorption where an electron switch is involved, is reserved for those cases where the dispersive forces are operative. The dispersive forces are those that exist between all molecules and which are due solely to quantum mechanical resonance of the electronic structure of the molecules involved. Even the noble gas atoms with spherical symmetry over a time average develop non-symmetric configurations due to the electronic zero-point motion. Evidence of this is the fact that the evaporation of a liquid or solid requires the expenditure of energy. This force is responsible for cohesion. Contact between two phases of different cohesive energies results in adhesion and such adhesion must exist between solid–vapour, solid–liquid and liquid–liquid interphases. Information as to the nature and magnitude of these forces can be gained from a study of each of these systems.

The calorimetric heats of physical adsorption of gases and of vapours on both high energy and low energy surfaces are comparable to the latent heats of evaporation, or the heats of adsorption are comparable with the cohesive energies of the adsorbates. The Langmuirian concepts of monolayer adsorption are not applicable here since, under conditions of temperature and pressure when adsorption can take place, condensation may also occur to build up a thick layer. The greater the disparity between the adhesion and cohesion the closer will the adsorption isotherm approximate to the Langmuirian form whilst, conversely, the smaller the difference and the closer the temperature to T_c, the two-dimensional critical temperature, the thicker the film. The presence of capillaries in the substrate results in capillary condensation more readily than on the plane surfaces. As a result, the isotherms for physical adsorption may take on various forms when v–P/P_0 plots are made, v being the quantity of adsorbate adsorbed as a liquid and P_0 being the vapour pressure of the liquid. The B.E.T. equation is customarily employed for determining the specific surface. This equation is based upon the premise that the bulk adsorption can be regarded as a series of superimposed monolayers each conforming to the Langmuirian conditions with suitable values for the two independent constants, α and ν, in the equation (Chapter 4). Clearly the premises of equilibrium between evaporation and condensation for each layer in a multilayer system are not tenable and, consequently, we are faced with two problems. Firstly, how thick must the layer be before the free surface acquires the property of the bulk liquid? Since the adhesive forces are contributing to the cohesion of the adsorbed vapour, they evidently extend beyond one molecular diameter but fall off with distance from the adsorbent. Secondly, we must inquire whether the condensed phase is to be regarded as a normal liquid or whether it possesses some structure.

The Potential Theory

Eucken, Williams and Polanyi were the first to develop a potential theory in which an interaction between the adsorbed molecule and the substrate occurred in an adsorption "volume", the adsorbate being regarded as a liquid. There exists, on this view, at any distance x from the surface, a plane of equipotential of adsorption ϵ_x. This potential is in fact the free energy change ΔG in an isothermal transfer of substance in the liquid state to the space in the adsorption volume, or,

$$\epsilon_x = RT \log \frac{P_0}{P_x}$$

If the law of attraction be written in the form

$$\frac{\partial \epsilon}{\partial x} = -\mu A_s^{1/2} A_v^{1/2} \phi(x)$$

where A_s and A_v are the cohesions of substrate and vapour respectively, that for the vapour being obtained from the van der Waals equation, we obtain

$$\epsilon = \int_{\infty}^{x_0} \mu A_s^{1/2} A_v^{1/2} \phi'(x)\,\mathrm{d}x = \mu A_s^{1/2} A_v^{1/2} \phi(x_0)$$

where x_0 is the depth of the adsorption space. The adsorption potential can be plotted against the weight of gas taken up to give characteristic affinity curves, and these should for any given substrate be dependent only on the square root of the cohesion of the gas. Each isopotential layer can be regarded as having a finite volume $\phi(x)$ and the total volume of the adsorption space is regarded as constant and at saturation to hold the same volume of liquid whatever its nature, i.e. $W_x/\Delta = \text{constant}$ where W_x is the weight of vapour adsorbed and Δ the density of the vapour as liquid at the temperature of measurement. Consequently, if the adsorbed liquid is regarded as incompressible $\phi(x) = W_x/\Delta = W_x\bar{v}$ where $\bar{v}$ is the molecular volume. Further, for any one value of ϵ_x the ratio of the amounts of vapour adsorbed at two different temperatures is equal to the ratio of the densities of the adsorbate at those temperatures. Experimental data on adsorption go far to support these views but, as Dubinin has pointed out, this hypothesis cannot be valid to include both surface and capillary condensation. On Polanyi's view the adsorption potential ϵ or ΔG is assumed to be temperature invariant, i.e.

$$\partial\left(\frac{\Delta G}{\partial T}\right)_{x,\bar{v}} = 0$$

Under these conditions the entropy of adsorption must be negative in sign, but the differential molar entropy of vapour adsorption $\Delta S = \partial(\Delta G/\partial T)_x$ is positive for multilayer adsorption. Taking the Kelvin equation

$$\Delta G = RT \log \frac{P_0}{P} = \frac{2\gamma\bar{v}}{r}$$

where γ is the surface tension of the liquid which wets the capillary and $\bar{v}$ the molecular volume at a constant degree of filling, we obtain

$$\partial\left(\frac{\Delta G}{\partial T}\right)_{x,\bar{v}} = \frac{2}{r}\left(\frac{\partial \gamma\bar{v}}{\partial T}\right)_{x,\bar{v}}$$