are drawn for $p=4$, 7, 22, and 112 plates. A curve for $p=337$ is indistinguishable from that for 112 plates. From these curves we may find the time required to reach any fraction of the maximum enrichment. Thus in a column with 22 plates, 70 percent of the final enrichment is reached, according to Fig. 2, at $(\tau)^{\frac{1}{2}}/22=7$, or $\tau=23{,}700$; that is, a time equal to 23,700 times the time required for an amount of material equal to that on one plate to be transported to the next.

The curves in Fig. 2 indicate that for columns with a large number of plates the curves become straight lines with a slope of 1.12 from zero up to approximately 60 percent of the maximum enrichment. This gives the simple formula for this range,

$$X_p/X_0=1+1.12\epsilon(\tau)^{\frac{1}{2}}.$$

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Surface Catalysis

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IT is the purpose of this paper to review some of the work of the author and his associates in the field of surface catalysis. This work was begun in a fundamental way through some experiments on positive ions[1,2] while the author was in residence at the California Institute of Technology. No complete discussion of the literature on the subject is attempted.

Perhaps most closely related to the author's earlier work at California Institute of Technology are some studies carried out in the middle thirties on the heterogeneous thermal decomposition of hydrocarbon molecules by a molecular ray method in which a beam of hydrocarbon molecules enters an otherwise closed vessel through an aperture (short channel) and sets up an equilibrium pressure of 10^{-5} to 10^{-6} mm Hg which could be measured with an accuracy of 10^{-9} mm Hg by a balanced high sensitive Pirani gauge circuit. The gauges could be maintained at any desired temperature including liquid nitrogen temperature. Inside the vessel was mounted an electrically heated platinum foil, the geometric arrangement of which was such that the incoming beam had to strike the hot surface, which was not much larger than the cross section of the beam—that is, not more than a few square millimeters. Since the total gas pressure, including the background pressure, was only of the order of some 10^{-5} mm Hg, gas molecules would only suffer collisions with the cold walls of the vessel except for about ten collisions with the hot foil before leaving the vessel altogether.

Some interesting results were obtained by this method. Saturated hydrocarbons dried over crystals of triphenylmethylsodium or fresh phosphorous pentoxide remained unaffected by the hot foil up to about 1600°C when they apparently decompose completely into atoms or such radicals as would be readily adsorbed on the cold walls of the vessel, reducing the pressure set up by the molecular beam to zero. A trace of water or hydrogen sulfide added to these gases would cause the beam molecules to be decomposed at much lower temperatures. These findings, which led to some practical application, were briefly reported in Nature[3] and are the basis of a patent[4] dealing with the influence of water or H_2S on the catalytic dehydrogenation of hydrocarbons. As it appears likely that a molecule such as water will be dissociated on the hot surface with subsequent temporary adsorption of the

[1] O. Beeck and C. Mouzon, Ann. d. Physik **11**, 858–62, 737–40 (1931); O. Beeck, Ann. d. Physik **18**, 414–16 (1933); W. Weizel and O. Beeck, Zeits. f. Physik **76**, 250–7 (1932); O. Beeck (review), Physik. Zeits. **35**, 36–52 (1934).

[2] O. Beeck, Proc. Nat. Acad. Sci. **18**, 311–13 (1932); O. Beeck and H. Wayland, Ann. d. Physik **19**, 129–42 (1934).

[3] O. Beeck, Nature **136**, 1028–9 (1935).

[4] O. Beeck, J. Burgin, and H. P. A. Groll, "Activating and maintaining the activity of dehydrogenation catalysts," U. S. Patent 2,131,089.

dissociation products which may well be protons and hydroxyl ions, it must be concluded that these adsorption products render the surface specifically active for the decomposition of the hydrocarbon molecules. This, indeed, is similar to the now slowly recognized fact that many powerful catalysts for hydrocarbon transformations such as polymerization, isomerization, alkylation, and cracking are activated by water which is naturally and unadvoidably present and thus renders these catalysts into so-called acid-type catalysts. The quantitative aspects of the molecular ray experiments appear to indicate that the primary decomposition of methane is into a hydrogen atom and a CH_3 radical and that of ethane into two CH_3 radicals. Permitting or assuming that CH_3 radicals survive many collisions with the cold walls of the vessel and have a long life and do not decompose further upon collision with the hot foil except at very high temperature—that is, if they behave as a gas under the experimental condition of extremely low pressure—we may then say the internal check of the two experiments with methane and ethane is perfect and many other results can be explained quantitatively. In an extensive study of reaction intermediates by means of a special mass spectrometer carried out by G. C. Eltenton[5] in the author's laboratory, the primary decomposition of CH_4 into CH_3+H and of C_2H_6 into two CH_3 radicals has positively been established and the relative inertness of these radicals, even at higher pressure and temperature, was demonstrated. Less readily explainable are the very reproducible results with molecular beams of acetylene unless the production of CH radicals which are stable under the experimental conditions are assumed. Eltenton[5] at least has brought proof that CH radicals are produced when acetylene molecules strike a hot carbon filament.

Of considerable interest is the observation in the molecular ray apparatus of the polymerization of olefins and acetylenes. Polymerization could be initiated by heating the foil in the path of the beam to a few hundred degrees C causing complete disappearance of the pressure produced by the beam. Lowering the foil temperature to room temperature would not interrupt this continuous polymerization process until—often after hours—the pressure caused by the molecular beam was gradually reestablished to its normal value, presumably through poisoning of the active ends of the polymerization chains.

In order to be able to make quantitative measurements with the Pirani gauges it was necessary to know the thermal accommodation coefficients for the various hydrocarbons and other gases on the Pirani gauge wires. A thorough study of these accommodation coefficients at the prevailing low pressures of 10^{-5} to 10^{-6} mm Hg over a wide temperature range was undertaken with the interesting result that the paraffin series could be represented accurately within the experimental error of less than 1 percent by the equation, $\alpha(C_{v0}+R/2)/M=\text{const.}$, where α is the accommodation coefficient, C_{v0} the specific heat per mole at constant volume for the ideal gas state, R the gas constant per mole, and M the molecular weight. This phase of the molecular ray work was fully reported in the *Journal of Chemical Physics*.[6]

While for purely thermodynamic reasons and for the purpose of avoiding subsequent and side reactions the thermal decomposition of hydrocarbons is often best studied at low pressures, the greatest number of the important catalytic reactions are of the type in which two or more molecules react to form a new compound and are best studied in the medium pressure range. Typical examples would be the catalytic oxidation, hydration, or hydrogenation of hydrocarbons, to name just a few. Here the transport of the reactants to the surface, diffusion into the pores, adsorption on the catalyst surface, the reaction step proper, desorption from the catalyst, diffusion and transport away from the catalyst surface will all have to be taken into account and complicate the kinetic picture of the reaction. Leaving the transport step out of the present considerations, the adsorption step is truly a crucial step in surface catalysis. Ethylene and hydrogen, for instance, will not react at room temperature in the gaseous state because too great an activation energy is required—that is, the potential threshold in this reaction is too high. When hydrogen is allowed to adsorb on a nickel surface the reaction is very fast even

[5] G. C. Eltenton, J. Chem. Phys. **15**, 455–81 (1947).

[6] O. Beeck, J. Chem. Phys. **4**, 680–9 (1936); **5**, 268–73 (1937).

at room temperature—that is, the activation energy has been lowered considerably. Calculation of the potential surfaces for such a reaction appears to be too difficult, if not impossible, with present quantum mechanical methods. Knowledge of the adsorption phenomenon in every individual case is of paramount importance. This includes the equilibrium coverage of the surface with adsorbed molecules or atoms in its dependence on pressure and temperature leading to the measurement of isotherms and isobars. As is well known to most physicists, the work of Langmuir is the basis for much of our present knowledge of the adsorption kinetics of monolayers. H. S. Taylor, introducing the concept of activated adsorption, has emphasized the activated state of the adsorbed molecule which may well be a complete dissociation into atoms. In the two extremes an atom or molecule may be adsorbed by van der Waals forces only (physical adsorption), or it may be incorporated in the surface as a known chemical compound such as an oxide or hydride. Actually, depending on temperature and gas pressure, any intermediate state may exist, and it is this intermediate state which is often particularly favorable for surface catalysis. It is evident that not only the atomic or molecular species of the surface but also the crystal structure must have a profound influence on the adsorption and, consequently, on the catalytic activity. With this in mind the author and his collaborators set out in the middle thirties to investigate just what this influence of crystal structure would be and chose as a suitable reaction the hydrogenation of ethylene over the metals of Group VIII of the periodic system. Aside from the hypothetical considerations of Balandin in 1929, there had appeared in 1932 a theoretical paper by Eyring and Sherman, who showed that lattice spacing should determine the activation energy of adsorption of gases. This was a challenge which now appears well worth the efforts expended.[7, 8, *]

To produce the catalyst the metals were evaporated onto a clean glass surface forming porous, highly active films. Electron diffraction experiments showed that the films were randomly oriented when evaporated in high vacuum and highly oriented when evaporated in an atmosphere of an inert gas at about 1 mm Hg pressure. Nickel, for instance, was completely oriented with the 110 plane parallel to the glass backing. Direct proof that the oriented film exposes the 110 face to the gas phase has recently been obtained by comparing the van der Waals adsorption of krypton and the chemisorption of hydrogen in which each hydrogen atom occupies one crystallographic site and in which the krypton atoms cover the whole film in close-packed fashion. It was found that the intrinsic or per unit area activity of nickel was five times greater for oriented than for unoriented films, showing the sensitivity of reaction rate to the spacing of the hydrogen atoms. Associating the activity with the 3.5A spacing of the 110 plane in the nickel lattice and relating this parameter of the other metals in Group VIII to their respective activities, highest activity could be predicted for rhodium, and the activity of this metal was indeed found to be several orders of magnitude higher than the lowest activity of the whole group of metals. The large spacing in rhodium of approximately 3.8A is also approximately the distance between the hydrogen atoms in opposite methyl groups of the ethane molecule. Furthermore, it was found that the activation energy E in Arrhenius' rate equation $k = Ce^{-E/RT}$ is the same (10.7 cal./mole) for all metals of this group, indicating that the large differences in rate are caused by a temperature independent entropy factor which—if we use the notation of the transition state theory of reaction rate—can be expressed by the equation

$$k = \kappa e^{[-(\Delta E^*/RT)+(\Delta S^*/R)]},$$

where the asterisk denotes the transition state. These results represent an interesting quantitative example of the importance of molecular geometry which is increasingly being recognized in many branches of chemistry, especially in biochemistry.

While these findings necessarily cause doubt in the earlier theories of catalysis with their emphasis on crystal lattice distortion or extra-

[7] O. Beeck, A. E. Smith, and A. Wheeler, Proc. Roy. Soc. A177, 62–90 (1940).

[8] O. Beeck, Rev. Mod. Phys. **17**, 61–71 (1945).

* The early work on this subject has been reported in detail (reference 12), and later work which was summarized recently (reference 13) will appear in several papers and in a monograph to be published by the Princeton University Press.

lattice aggregates of atoms with abnormal activity, they do not necessarily eliminate the active center theory based on inhomogeneity of the surface. In fact, it appears certain that in the more complicated catalyst systems consisting of several compounds inhomogeneity of the surface may be important.

There are some other aspects of the metal film work which may be of interest. It was, for instance, discovered that with mixtures of acetylene and ethylene, acetylene will be hydrogenated selectively before ethylene is attacked. Not only was this phenomenon satisfactorily explained on the basis of preferential adsorption but its application led to large scale removal of vinyl acetylene from butadiene in the manufacture of synthetic rubber.

If the metal films are thick enough, diffusion into the pores has to be taken into account, and investigation of this led to the discovery of anomalous diffusion effects which can only be explained by a rapid transport of gas in the adsorption layer.

As has become evident from the foregoing, the actual seat of surface catalysis, namely the surface proper, is relatively elusive to both physical and chemical methods. Adsorption methods have been most successful in the past and are now being complemented by other physical methods, among which magnetic methods appear to be particularly promising. X-ray and electron diffraction methods are used for investigation of the bulk properties of catalyst materials which are, of course, closely connected to the surface properties. In the early stages of the war, for instance, repeated failure of a catalyst used in the so-called hydroforming process was traced by crystal structure analysis methods to be due to the thermal transformation of alumina (used as support for molybdenum oxide) from the β-form into the α-form, and further crystallographic studies led to the development of thermo-stable catalysts.[9]

Aside from the physical methods directly applicable to the catalyst, most of the modern studies in catalysis would be impossible without the new physical methods of analysis such as mass spectrometry and absorption spectrophotometry in the infra-red and ultraviolet which have completely revolutionized the field of hydrocarbon analysis and several of which have been pioneered by the physics staff at Shell Development Company.[10]

Last, the application of the isotope tracer technique to the problems of catalysis will be briefly mentioned. By use of one of the earliest samples of tritium made available through the Radiation Laboratory at the University of California, it was shown in the author's laboratory before the war that the rate of isomerization of *n*-butane to isobutane over aluminum chloride activated with water containing tritium was proportional to the rate of tritium exchange with the hydrocarbon. This clearly demonstrated that the activation of the isomerization reaction took place through an attack of the carbon-hydrogen bond. Subsequent careful investigation showed that water was indispensible in this reaction.[11] Recently the isomerization of butane to isobutane was shown to be intramolecular with respect to the carbon skeleton by isomerizing *n*-butane containing C^{14} in the presence of propane and finding that no C^{14} could be found in the propane. Believing that the intramolecular isomerization of hydrocarbon within a straight chain should be possible, the isomerization of propane with C^{13} in the end position was investigated over moist aluminum bromide with the result that this isomerization proceeds with the same rate as the *n*-, isobutane isomerization over the same catalyst.[12] The intramolecular character of this reaction is clearly demonstrated by the fact that no propane molecules containing two C^{13} atoms could be detected even after 600 hours over the catalyst. Since the isomerization conditions are mild as compared with the conditions for most other hydrocarbon reactions or transformations, these findings should be of great importance in the study of reaction mechanisms by the tracer method.

[9] A. E. Smith and O. A. Beeck, "Preparation of an alumina supported molybdenum oxide catalyst," U. S. Patent 2,422,372; "Thermostable catalysts for the dehydrogenation of hydrocarbons," U. S. Patent 2,422,172.

[10] R. R. Brattain and O. Beeck, J. App. Phys. **13**, 699–705 (1942); R. R. Brattain, R. S. Rasmussen, and A. M. Cravath, J. App. Phys. **14**, 418–28 (1943).

[11] D. P. Stevenson and O. Beeck, to be published shortly in J. Am. Chem. Soc.

[12] O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, Phys. Rev. **73**, 537 (1948).