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A THEORY FOR THE ACTIVITY OF CONTACT CATALYSTS

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During a study of the reaction of hydrogen and oxygen at low pressures on platinum wires[1] the observation was made that the activity of the wire was a function of the difference in temperature between the wire and the wall of the reaction tube. The pressure was such that the mean free path of the molecules was greater than the distance from the wire filament to the wall of the tube. If the wire and tube were at the same temperature the reaction would not proceed. When the wire was heated 50 to 100° higher than the temperature of the wall a reaction occurred. This was true for wall temperatures ranging from −180 to +200°. If a reaction was progressing, its speed would be increased merely by cooling the wall, and retarded if the wall temperature was made to approach the wire temperature. Appropriate experiments proved that this peculiar effect was not due to gas concentration, nor to the rate at which water vapor was removed from the reaction tube. The vessel wall had no catalytic effect since it made no difference whether the wall was Pyrex, fused silica, aluminum or molybdenum oxide-coated Pyrex. There was no alternative to the conclusion that the reaction rate was a function of the dissipation of energy from the catalyst wire, or, in other words, of the difference in temperature between the catalyst wire and the vessel wall. This conclusion led to a modified concept of catalytic activity.

Accurate measurements of the amounts of energy supplied to the wire were made as follows.

A small resistance of 0.30 ohm was connected in series with the catalyst. The construction of this resistance was such that its temperature would not depart appreciably from room temperature during the course of the experiment. A Leeds and Northrup thermocouple potentiometer was connected across this resistance as shown in Fig. 1. This arrangement furnished a precision null method by which the current through the catalyst arm of the Wheatstone bridge could be determined without disturbing the Wheatstone bridge balance.

As an example of the data obtained the voltage across the auxiliary resistance was found in a typical experiment to be 19.4 millivolts when the bulb of the catalyst tube was at 23°. The current flowing through this arm of the Wheatstone bridge was therefore 0.0647 ampere. Since the resistance of the catalyst filament was at that time 9.00 ohms (correspond-

[1] H. G. Tanner and G. B. Taylor, THIS JOURNAL, **53**, 1292 (1931).

ing to 100°), the power supplied to the filament was 0.0377 watt. When liquid air was placed around the bulb the current through the catalyst arm of the Wheatstone bridge had to be increased to 0.138 amp. in order to maintain the catalyst resistance (average temperature) constant at 9.00 ohms. The power, therefore, was 0.171 watt. The ratio of these two wattages is as 1 is to 4.5. This means that four and a half times as much energy was being dissipated from the wire when the bulb was at −180° as when the bulb was at room temperature.

The ratio of the energies dissipated with bulb at room temperature and at liquid air temperature varied not only with the gas pressure, the nature of the gas and other obvious factors, but also with the condition of the wire surface. The higher the catalytic activity of the wire the greater the effect of the bulb temperature upon the rate of reaction, and upon the abnormal cooling of the filament. These observations show that an intimate connection exists between thermal accommodation coefficient and catalytic activity and indicate that the accommodation coefficient itself may be a function of temperature difference.

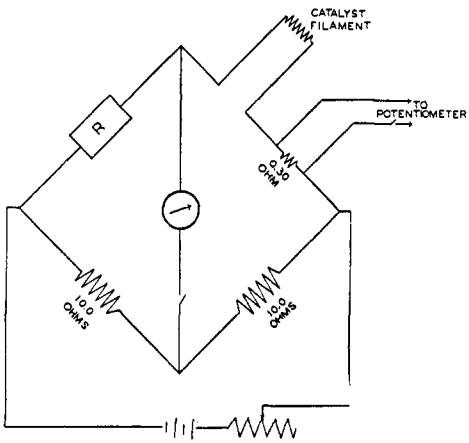

Fig. 1.—Diagram of electrical connections.

It may be mentioned that the peculiar effect of bulb temperature upon the heat transfer from the wire was proved to depend upon the gases present and not upon the filament end-losses, or radiation. When the bulb was exhausted to a pressure below 1×10^{-6} mm., the heat losses from the filament were practically independent of the bulb temperature.

Speculations about catalytic activity frequently have been concerned rather with the mechanism of catalytic activation than catalytic activity in the strict sense of the term. Catalytic activity is an expression of the efficiency of a catalyst, and it should always be distinguished from the mechanism of catalytic activation. Concepts such as "elementary spaces," "stretched molecules," etc., assist in giving a definite picture of the way in which adsorption may occur, and how certain areas on a catalytic surface activate molecules, but these concepts are not sufficient to account for the difference in activity of two or more catalysts which may be chemically identical. This difference in activity has always been regarded as due to a difference in the number of active spots exposed. There is another possibility, however, which is worthy of consideration, *e. g.*, the rate

at which the active spots function. The efficiency of the active spots rather than their number may be the controlling factor.

The mechanism of adsorption plays a prominent part in current theories of catalysis. Although adsorption undoubtedly is of great importance, yet a catalyst functions only when molecules get up to the active spots, react, and the reaction products depart. Adsorption is but a part of this process. In a sense, a catalyst (more accurately the active spots) must "breathe" in order to function. Current theories stress adsorption, but give little or no consideration to the "exhalation" part of the cycle. The complete cycle of "respiration" and the rate of its occurrence are fully as important as the mechanism of adsorption.

The respiratory action is explained in this paper by assuming that the active spots fluctuate in temperature. During moments when one of them is below the average temperature, adsorption occurs. A little later this spot becomes hot (from Brownian motion of adjacent molecules, or chemical reaction, etc.), and the adsorbed molecule departs as a different chemical entity. When the spot has cooled the process repeats. From this viewpoint, catalytic activity is governed by those forces which control the temperature fluctuations of the active spots.

In the experiments above described no reaction occurred, for example, when the wire and wall were both at 100°. Maxwell's law of temperature probability could be applied to any given atom on the wire surface because a condition of thermal equilibrium existed. The probability that an atom departed a hundred degrees, say, from the average temperature was very small. Maxwell's law cannot be applied, however, when thermal equilibrium does not exist. It is not applicable to "steady state" conditions. When, in the experiment, the bulb was cooled by liquid air, gas molecules at −180° struck the filament whose average temperature was maintained at 100°. The probability that a given atom on the filament would be at 0°, for instance, was very much increased. The average temperature of the filament, however, was forcibly maintained at 100°. Therefore the probability of a given atom on the filament having a temperature of 200°, say, was greatly increased, as compared to thermal equilibrium conditions. In other words, for a given degree of probability, an atom on the wire surface fluctuated through a wider temperature range. The "time-lag" of gas molecules striking the filament was increased by their having a lower temperature at the moment of collision, and the probability of their subsequent activation, reaction and desorption was increased by their attainment of the postulated abnormally high temperatures. The rate of "respiration" of the active spots was increased because their fluctuations in temperature were either extended, or, for a given temperature change, made more rapid. The increased reaction rate which accompanied the temperature difference in the experiments described above is therefore explained.

The rate of clean-up of certain pure gases by hot filaments was found by I. Langmuir[2] to be increased when the temperature of the bulb was lowered. Nitrogen, for example, was cleaned up by a hot molybdenum filament very rapidly when the bulb was cold. Langmuir's explanation for the bulb-temperature effect was built upon the assumption that the rate of evaporation of the molybdenum was independent of the bulb temperature. The increased rate of clean-up was attributed to a higher reaction efficiency per collision of molybdenum vapor molecules and nitrogen when the bulb temperature was low.

An alternative explanation can be offered from the viewpoint of the hypothesis developed in this paper by assuming that the rate of evaporation of molybdenum was the controlling factor involved, and that this rate was affected by the temperature of the bulb. When a cold molecule of nitrogen struck the filament, a cooling effect occurred at that point. Since the average temperature of the filament was kept constant, an adjacent atom of molybdenum must therefore have acquired an abnormally high temperature. Since the rate of evaporation of molybdenum was shown by Langmuir to be an exponential function of temperature with a high coefficient, the greatly increased rate of evaporation from the abnormally high temperature areas would produce a net increase in the gross rate of evaporation. The greater amount of molybdenum vapor produced would of course account for the increased rate of reaction with nitrogen. If this interpretation be accepted there appears to be no fundamental difference in the effect of bulb temperature in these clean-up experiments, and in the catalytic experiments just described. Conversely, the fact that two independent examples of the bulb-temperature effect can be explained on a common basis lends support to the theory.

In the ordinary use of a catalyst the abnormal temperature fluctuations of the active spots are probably set up by any condition capable of disturbing thermal equilibrium. Adsorption desorption, and chemical reaction, for example, are processes involving large heat changes. Each of these processes would greatly disturb the normal Maxwellian variation of temperature of an active spot. An active spot may momentarily attain a temperature many degrees, perhaps many hundred degrees in case of gases, above or below the average temperature. Even when a liquid surrounds a catalyst, as for example an oil around nickel-on-kieselguhr, Armstrong and Hilditch[3] found evidence that some of the nickel particles during hydrogenation must have attained a temperature above 300°, although the oil appeared always to be below 180°. This is significant, because it means that the particles of nickel fluctuated in temperature between these limits at least.

[2] Langmuir, THIS JOURNAL, **41**, 167 (1919).

[3] Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **A108**, 111 (1925).

If the foregoing postulates concerning the temperature variation of active spots and catalytic activity be granted, other catalytic phenomena can be explained with the help of a few minor postulates. The beneficial effect of a rough surface, for example, is easily explained provided one grants that temperature oscillations are greater for an active spot located on a spire of a rough surface compared to the temperature variations of an active spot on a smooth surface. This assumption is not unreasonable because an atom located on the tip of a microscopic spire has less chance to stay in thermal equilibrium with its surroundings than an atom lying on a smooth surface.

The difficulty of correlating catalytic activity with adsorption can likewise be explained. Porous substances are good adsorbents. Some of them are good catalysts. Adsorption, however, is unidirectional and not "respiratory" or cyclic in character. Furthermore, adsorption probably occurs to a major extent *within* the capillary spaces of a porous substance, whereas catalysis is postulated to occur *on* the surface, *e. g.*, on the projecting spires at the mouths of the capillaries. A porous material may be one having capillaries highly branched within the body of the substance, or it may have a capillary structure such that most of the capillaries are short, and terminate on the external surface. The former would not be as rough a surface as the latter, but would probably adsorb a greater quantity of material. Porosity and roughness are therefore related. Similarly, adsorption and catalytic activity are related, but the relationship in either case will always evade any general quantitative treatment.

There is nothing in this explanation which would preclude some catalysis occurring in the depths of the capillaries of a porous substance, but in view of the respiratory nature of catalysis, and the slow rate of diffusion into and out of tiny capillaries, the interior surface of any capillary less than 1000 Å. in diameter probably plays but a minor role.

Catalyst supports must profoundly influence the temperature variations of the catalyst particles distributed thereon. When nickel oxide is precipitated on kieselguhr, for example, and subsequently reduced, the nickel does not form a continuous surface. The catalyst support protrudes here and there all over the surface. Ultramicroscopic specks of nickel are "imbedded" in a thermally different material. This heterogeneity of the surface is favorable to large temperature fluctuations of the nickel specks. A reaction occurs on a speck of nickel, thereupon the temperature is raised perhaps a hundred degrees or more.[3] If this heat be not dissipated too rapidly, desorption occurs. Later the speck cools so that adsorption and reaction can again occur. Were it not for the thermal insulating effect of the catalyst support, the nickel speck could not attain as high a momentary temperature. A spot on massive smooth nickel would, in comparison, stay nearly constant in temperature because of the easier exchange of energy with neighboring atoms.

Promoters which do not act chemically may function by increasing the physical heterogeneity of the surface, and thereby accentuate the local temperature fluctuations. Clean liquid surfaces rarely, if ever, function as heterogeneous catalysts. The reason for this may well be that the active spots (elementary spaces) maintain a relatively uniform temperature.

Electron emission from heated filaments varies exponentially with temperature, and is always observed under thermal conditions far removed from equilibrium. Therefore, the concept of abnormal surface temperatures developed above may find application in explaining some of the peculiarities of electron emission. Roughness of surface, the rate of heat transfer from core metal to oxide coating, and a heterogeneous ("promoted") surface may each be factors to be considered. A study of the flicker effect[4] with variation in the temperature of the gas striking the filament might yield information of value in substantiating or refuting the above developed theory, especially if K. H. Kingdon's[5] suggestion that the flicker effect involves surface temperature fluctuations is found to be true.

Summary

Catalytic activity is postulated to depend upon the rate at which active spots function.

The action of an active spot is regarded as respiratory in character, and dependent upon fluctuations in temperature of these spots.

The concept of "average temperature" is discussed, and the probable thermal behavior of rough, heterogeneous surfaces is contrasted with that of smooth, homogeneous surfaces.

These concepts afford a partial explanation of variations in catalytic activity occasioned by promoters, supports, roughness of surface, porosity, etc.

The suggestion is made that electron emission may be influenced by the same thermal conditions which affect catalytic activity.

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[4] G. B. Johnson, *Phys. Rev.*, **26**, 71 (1925); W. Schottky, *ibid.*, **28**, 74 (1926); I. Langmuir and K. H. Kingdon, *ibid.*, **34**, 129 (1929).

[5] Kingdon, *ibid.*, **37**, 89 (1931).