

## *Wilhelm Ostwald, "Catalysis"*

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The phenomena summarized by Berzelius are the following: the transformation, discovered in 1811 by Kirchhoff, of starch into dextrin and sugar by boiling with dilute acids; the same effect of malt extract, also demonstrated by him in 1813; the partial isolation, carried out in 1833 by Payen and Persoz, of the substance that is active in this process, namely, diastase; the decomposition, investigated in 1818 by Thenard, of hydrogen peroxide by metals, oxides, and by fibrin; the effect of platinum on combustible gas mixtures (J. Davy, 1817, and Döbereiner, 1822); and finally, as a result of the above-mentioned experiment by Mitscherlich, the formation of ether.

These processes have in common that they are brought about by the presence of substances whose components do not appear in the end products and which therefore are not used up in the reaction. Accordingly, Berzelius defines them as follows: "The catalytic power essentially appears to consist in the fact that substances are capable, by their mere presence and not by their affinity, of eliciting the affinities which are dormant at this temperature, so that, because of them, the elements within a composite substance arrange themselves in other relationships by which greater electrochemical neutralization is produced."

### **Catalyses in Homogeneous Mixtures**

... The group of contact effects to be discussed now is the largest and most important theoretically. Most of the innumerable catalytic effects discovered in the intervening time belong in this category.

If we ask whether the explanation given for the first case is applicable here, also, the answer must be negative. The essential feature in the first case was the occurrence of the new phase; but this is excluded here by the definition.

We find the correct point of view for the new problem if we adhere to the general condition that has just been postulated for all systems that are subject to a contact effect; it shall not represent a stable state, for such a state cannot experience any change without the addition of energy. But what is the behavior of unstable structures when they are homogeneous?

The answer is that homogeneous, unstable structures (i.e., assemblies of substances) cannot exist other than in a state of transformation. A supersaturated solution can, if the supersaturation remains within certain limits, be stored with appropriate safeguards for an unlimited time, and no change will occur in it. However, a liquid that, without the addition of free energy, can yield other liquid products that remain in solution cannot be stored without forming these products. This may take place extremely slowly—so slowly that no change can be demonstrated at all without prolonged special study directed toward this purpose. But the most reliable foundations known to us for general conclusions—namely, the energy laws—demand that the transformation actually take place. They dictate no numerical value for the speed that must be maintained in the process; they only require that this speed shall not be strictly zero, but have a finite value.

In this way, we at once obtain the definition of a catalyst for this case, also: "A catalyst is any substance which, without appearing in the end product of a chemical reaction, alters its speed."

The first theory of catalytic phenomena was formulated by Liebig for the purpose of making the concept created by Berzelius appear superfluous. Liebig conceived of catalysis as a direct consequence of the mechanical law of inertia. His statement says: "This cause is the capacity, possessed by a substance engaged in decomposition or

combination, i.e., in chemical action, of eliciting in another substance in contact with it the same chemical activity, or making it capable of undergoing the same change which it experiences itself. This capacity is best exemplified by a burning substance (one engaged in action) through which we elicit the same activity in other substances by bringing them near the burning one.”

Obviously, Liebig’s explanation was rather unfortunate. His own example defeats him, for to ignite something one does not need a burning substance, but merely a hot one; it is entirely irrelevant for the result whether it is hot due to a chemical process or for any other reason (e.g., due to an electric current). Such objections were indeed raised, and Liebig had cause to formulate his hypothesis differently. He explained his view in the following words in connection with the question of the fermentation of sugar:

“Heat is capable of eliminating the static moment in the elements of many chemical combinations. Similarly, this occurs by means of a substance whose elements are themselves in a state of eliminated equilibrium; the motion in which its atoms are engaged is imparted to the atoms of the elements of sugar; they no longer remain in the state in which they form sugar, but order themselves according to their special affinities.” ....

That the whole matter actually had entered a dead-end track because of the hypothesis of molecular vibrations is seen from the fact that the problem which, at one time, had been treated with such great zeal did not subsequently become the subject of any sustained scientific study. For a long time, only isolated investigators concerned themselves with catalytic phenomena, observing and describing them. Schönbein, to whose investigations we owe so many of the facts that we know at this time, did not participate in the theoretical disputes about their causes; instead, it was an evident pleasure for him to pursue these phenomena which contemporary chemistry, for which he had little regard, did not explain or classify.

Another thought that had been postulated much earlier but had not gained acceptance for a long time presents a much more favorable picture. This is the idea of intermediary reactions.

It had its origin in the first scientific treatment given the chemical reactions in a lead chamber during the sulphuric acid process. In an investigation which has remained a classic, Clément and Desormes, in 1806, provided the explanation that is still generally accepted today for the effect that the oxides of nitrogen have in the oxidation of sulphurous acid by the oxygen in air. As all of you know, this is based on the assumption that sulphurous acid is oxidized by the higher oxides of nitrogen, while these are transformed into nitrogen. The latter again combines with the oxygen of the air, and the reaction can again take place. Thus, a small quantity of nitrogen oxides serves to oxidize unlimited quantities of sulphurous acid.

It is strange that this case was not even discussed at the time of the dispute between Berzelius and Liebig. It was not until later that applications of the old point of view were found to other cases in which chemical reactions are accelerated by certain auxiliary substances, although there is no stoichiometric relationship with these. But gradually this concept became more and more widespread, and today it must be regarded as the oldest and most important attempt to explain certain, though perhaps not all, catalytic processes. ...

Assuming that the appropriateness of the theory of intermediary products has been demonstrated in individual cases (this will happen, according to all indications), a new question now arises; namely, whether this provides an explanation of all catalytic processes. I believe that the answer to this must be an unconditional no. I believe that I know a considerable number of catalytic processes to which such an explanation is not applicable. In particular, I see no possibility that the delaying catalytic effect could be explained by means of intermediary products. If a reaction proceeds more slowly through the

intermediary products than in the direct way, it will take place by the latter, and the possible existence of intermediary products has no effect whatever on the process. ...

A more complicated case of catalytic phenomena is that of processes in which the substances participating in the reaction have an additional catalytic effect themselves. Among the available possibilities of autocatalysis, I only want to mention the case in which an accelerator may be created by the reaction itself. For example, this occurs in one of the best-known reactions, the solution of metals in nitric acid. The nitrous acid thus produced greatly accelerates the velocity of action of the nitric acid, and thus the following phenomenon comes about:

If the metal is placed in pure acid, the reaction begins extremely slowly. As it progresses, it becomes faster and finally violent. When this period has passed, the process slows down and ends with a velocity converging toward zero.

This is in noticeable contrast to the usual course of reactions, which start with the maximal velocity and, because of the gradual consumption of the effective substances, become progressively slower.

In this connection, physiological analogies intrude irresistibly; this is a typical characteristic of fever. And still another important physiological fact can be illustrated in the same way: habit and memory. I have here two samples of the same nitric acid, which differ only in the fact that I previously dissolved a small piece of copper in one of them. I now introduce two identical sheets of copper into the two acids, which are standing in the same water container so that they have the same temperature. You can see at once that the acid that had already dissolved copper has become "accustomed" to this work and starts to carry it out very skillfully and quickly, while the inexperienced acid does not know what to do with the copper and executes its action so sluggishly and awkwardly that we cannot wait for it. That this is a case of catalysis by nitrous acid becomes evident

when I add some sodium nitrite to the sluggish acid: here, too, the copper is at once attacked and dissolved.

### **Heterogeneous Catalysis**

The best-known case of heterogeneous catalysis is the effect of platinum on combustible gas mixtures. Previously, the phenomena occurring in detonating gas were of prime interest; now, for practical reasons, the combustion of sulphur dioxide into trioxide has become the most important.

All these cases, also, probably involve accelerations of slow reactions, even though it has to be admitted that in detonating gas, for example, the formation of water at ordinary temperatures without a catalyst has not yet been demonstrated.

But the steadiness of the change in velocity with the temperature in this case justifies us in assuming that there is indeed a very low reaction speed even at ordinary temperatures. That it is so particularly low is in keeping with the general fact that all reactions of gases take place at a relatively very low speed.

This important fact is clearly evident, for example, in the experiments of Berthelot and Péan de Saint-Gilles. A comparison of ester formation from acid and alcohol at the same temperature was made in two experiments, the substances used being liquid in one case and gaseous in the other. The experiments do not lend themselves to precise calculations; but the question is not whether the slowing down can be completely explained by the great decrease of concentrations or whether (as is more likely) there is a more significant meaning; it is sufficient to know that the reaction velocity was depressed to about a thousandth by the transition into gaseous form.

It is possible to use this as a basis for a theory of the above mentioned accelerations (Bodenstein). If we imagine that, at the existing temperature, a part of the gaseous system is transformed into the liquid state, or if we assume a density corresponding to this state, the reaction will occur more rapidly in this portion, and the liquid components of the

initial substances will be transformed into the end products. Now, if the liquefying or compressing agent is so constituted that it compresses new quantities of the initial substances after the first compressed portion is used up, then these again will react quickly, and so on; the result is an acceleration of the reaction. Such an effect on the gases due to platinum is quite possible.

I do not want to assert with this explanation that platinum catalyses actually take place in this way, but only wish to point out that there is a possible way in which they could occur. We then would have the simplest and purest case of the accelerating intermediary reaction, to which I have referred earlier.

As Professor [Georg] Bredig explained to me verbally a short time ago, the mechanism of such an acceleration can be made clear in terms of a liquid medium in which small amounts of another liquid are suspended. If this suspended liquid has such a property that the reaction of the substances present occurs more quickly in it than in the main mass, the components of the reagents present there would be transformed first. The product would diffuse into the surrounding liquid; likewise, new amounts of the reagents would enter, since the concentration of the different substances always becomes uniform by diffusion. In this way, the entire amount of reagents would gradually make its way through the suspended liquid and react there; the result is an acceleration of the reaction.

The material presented here can perhaps also be applied, according to Bredig, to the case in which the catalyst is present in the liquid in the colloidal state. As is well known, Professor Bredig and his students, in a series of excellent experiments, have demonstrated and measured a great variety of the most

energetic catalytic effects that can be produced by colloidal platinum that he made and by other colloidal metals. He has also emphasized repeatedly that the catalysts that occur naturally and are so very effective—namely, the enzymes—likewise are in a state of colloidal solution or suspension.

These observations, again, make no claim other than that of being conjectures that can be tested experimentally. However, I should not fail to direct your attention to the fact that it has become possible only through the concept of catalysts as accelerators that one can even postulate such conjectures that can be tested scientifically. I ask anyone to attempt something similar by means of molecular vibrations.

### The Enzymes

Berzelius had no doubt that the conversion of starch into sugar by acids is to be put side by side with the conversion by malt extract. Payen and Persoz had the same idea; they isolated the effective substance, diastase, or at least produced it in concentrated form. The same holds for Liebig and Wöhler, who, in an outstanding experiment, studied the decomposition of amygdalin under the catalytic influence of emulsin.

The more recent investigations on the laws of enzyme action have, in my estimation, yielded nothing that would cause one to postulate any basic difference between the two types of action. On the contrary, Bredig's experiments, mentioned above, have made it possible to find much more thorough agreement than was to be expected.

We may thus regard the enzymes as catalysts that are created in the organism during the life of the cells and through whose action the living being disposes of the greatest portion of its tasks.

<sup>1</sup>[Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New

York, 1966, pp 204-212. Translation by Elisabeth F. Lanzl. —CJG]