Ammonium hydroxide with an error not greater than 0.105%
Ammonium sulfide   with an error not greater than 0.015%
Potassium ferrocyanide with an error not greater than 0.009%

provided the volume of the electrolyte was 100 cc. and there was originally present one gram of copper.

III. The recommended procedure for the detection of traces of copper at the end of electrolytic copper precipitation in the kinds of solutions indicated, is as follows: Take one cc. of the sample in a narrow test tube constructed as described. Make alkaline with ammonium hydroxide, acidify with glacial acetic acid, and add two drops of 2% $K_4Fe(CN)_6$ solution. A pronounced red color indicates more than 1 mg. of copper. Make similar additions to another tube as a blank, replacing the sample to be tested by distilled water. If by comparison the tubes are practically of the same color, then there is present not more than 0.1 mg. of copper in 100 cc. of the solution.

LABORATORY OF INDUSTRIAL CHEMISTRY.

OUTLINE OF A THEORY OF HOMOGENEOUS CATALYSIS.[1]

BY M. A. ROSANOFF.

The word catalysis was introduced about eighty years ago by Berzelius. It grouped together phenomena that had up to that time remained unconnected. But while a great and increasing number of new catalytic phenomena were discovered in subsequent years, the concept itself remained vague until Ostwald introduced his well known definition based on the conception of velocity of chemical change—a conception which was born with modern chemical kinetics and was unknown to Berzelius. According to Ostwald, a catalyzer is a substance whose presence *hastens* a given chemical reaction, although the reaction would also take place in its absence. Ostwald believes that a catalyzer exists for every reaction and, conversely, that any given substance is capable of catalyzing some reaction.

The object of the present communication is to tentatively propose some modifications of this conception of catalysis. The ideas formulated here will sound partly familiar, partly more or less new. What I have attempted to do is, to construct a theory involving few hypothetical assumptions, yet definit enough to be of practical service as a working-theory, or at least as a basis for further discussion. Only experimental research can really prove or disprove a theory of this type, and I should not take the liberty of publishing the present outline if its ideas were not

supported by a series of experimental studies carried out in these laboratories during the past four years. These studies, now ripe for publication, will appear as soon as their final redaction is completed.

1. In the first place. I propose to classify homogeneous catalysis into direct, or chemical, and indirect, or medium-catalysis, as follows:

A *direct catalyzer* is a substance (or molecule) which *takes part in the reaction* but does not appear in the stoichiometric equation. In other words, it is a substance whose influence on the reaction depends on the formation of intermediate molecular complexes.

An *indirect catalyzer* is a substance which, without itself taking part in the reaction, influences its velocity by affecting the particular conditions upon which the mechanism of the given reaction may depend—say, the association (*i. e.*, formation of complexes) or dissociation, as the case may be, of the reacting substances proper. These conditions are well known to be influenced by the nature of the medium; and as the nature of the medium is determined by each and all substances present, the reagents and products of the reaction, as well as the solvent or solvents, neutral salts, and other non-participants, it is obvious that *all* substances are indirect catalyzers of *all* reactions.

2. Since a direct catalyzer takes part in the reaction by forming intermediate molecular complexes, direct catalyzers will obey the law of mass action as strictly as do the molecules appearing in the stoichiometric equation.

3. Since an indirect catalyzer does not itself react chemically, it cannot be expected to obey the law of chemical mass action. In fact, in a series of cases of catalysis investigated in these laboratories I have found the experimental facts to be represented with great precision by an equation entirely different from the equation of mass action.

This catalysis equation is based on the assumption that *the relative change of the velocity coefficient of a reaction is proportional to the change in the concentration of the indirect catalyzer* (a form of the compound interest law). In symbols:

$$d \ln k / dC = \kappa \text{ (constant)}.$$

Putting $k = k_0$ when $C = 0$, we get, by integration,

$$k = k_0 e^{\kappa C}.$$

If we take into account the concentrations C_1, C_2, C_3, etc., of all the substances present, we get:

$$k = k_0 e^{\kappa_1 C_1 + \kappa_2 C_2 + \kappa_3 C_3 + \cdots},$$

in which case k_0 represents the reaction velocity altogether freed from the influence of medium. This may be thought of as the reaction velocity in the gaseous state at infinit dilution.

4. Indirect catalyzers must invariably follow Ostwald's principle,

that catalyzers do not render reactions possible, but merely hasten them. According to the above catalysis equation, if k_0 were zero, the velocity coefficient k would likewise be zero for all finite concentrations of the catalyzer.

5. On the contrary, direct catalyzers will *not* obey the Ostwald principle. Since they follow the law of mass action, the observed reaction velocity will be proportional to their concentration, or to some integral power of the concentration, and hence for zero concentration of the catalyzer the reaction velocity itself will be zero. Thus, it seems beyond doubt that the decomposition of amyl esters cannot take place at all in the absence of acid.

Apparent exceptions to this are presented by cases like the hydrolysis of methyl acetate by acids or bases. But here the possibility of the reaction is due to water itself being a weak base.[1] When acid is present, two reactions go on simultaneously: one directly catalyzed by the acid, the other directly auto-catalyzed by the ionized part of the water. When the acid is removed, the second of these reactions takes place alone.

6. The effect of an indirect catalyzer is purely relative. A substance S_2 introduced into the medium of the reaction in place of a substance S_1 may hasten the reaction. Then S_2 would appear as a positive catalyzer with respect to S_1, while S_1 would appear as a negative catalyzer with respect to S_2. It may happen that the catalytic effects of S_1 and S_2 are equal, but then both will be positive catalyzers with respect to some third substance S_3, or negative with respect to some fourth substance S_4, that may be present in the medium of the reaction. In all such cases an indirect catalyzer is conceived as merely affecting the molecular state of the reagents. If a given substance should exert a retarding effect by forming an inactive compound with one of the reagents, it could hardly be classed as a catalyzer: one might as well remove the reagent by precipitation and speak of the precipitation as a catalytic process. Of course, the detection of such elimination of reagents is none the less interesting.

In accordance with the principles just stated, the number of possible indirect catalyzers for any given reaction is indefinitely large, and *all negative catalyzers belong to this class*. On the other hand, direct catalyzers (because governed by the law of mass action) can only be positive.

From the viewpoint of our theory, it is plain that the velocity of chemical reactions is governed, not by the law of mass action alone, but by two laws simultaneously: the law of mass action and a catalysis law. Assuming the catalysis law to be generally expressed by the equation proposed above, we, therefore, have:

[1] See Wijs, *Z. physik. Chem.*, **11**, 492; **12**, 514 (1893).

$$\frac{dx}{dt} = \frac{k_0}{z^m + n + \ldots -1} \cdot e^{\kappa_1 S_1 + \kappa_2 S_2 + \ldots} \cdot (a - x)^m (b - x)^n$$

$$- \frac{k'_0}{z^{m'} + n' + \ldots -1} \cdot e^{\kappa'_1 S_1 + \kappa'_2 S_2 + \ldots} (a' + x)^{m'} (b' + x)^{n'},$$

where S_1, S_2, etc., stand for the concentrations of the several substances present, including both those taking part in the reaction and the non-participants.

An equation involving so many constants as this would be almost worthless for purposes of experimental verification of its underlying theory. But, fortunately, reactions are usually carried out in moderately dilute solutions. In these, the disappearance of reagents and the appearance of reaction products have no appreciable influence on the solvent exponent κS, which remains constant, and thus during a single process the complex equation just given turns into the ordinary equation of mass action. If the same reaction is next carried out with the concentration of one of the substances (say, the solvent) considerably increased or decreased, the reaction will be found to have a new constant coefficient of velocity. But these coefficients (k), remaining constant during a single process but changing from process to process, will be determined by the catalysis equation

$$k = k_0 e^{\kappa S}.$$

Thus only one indirect catalyzer will be involved under ordinary physico-chemical conditions, and, therefore, the practical application of the catalysis equation will be simple. Its verification will be the easier as by a simple transformation it shows the logarithm of the velocity coefficient to be a linear function of the concentration of the indirect catalyzer. In view of the constancy of $k_0 e^{\kappa S}$ during a single process, the catalysis equation will be applied after the velocity coefficients have been obtained by integrating the differential equations of mass action as usual.

For the equilibrium of balanced reactions, assuming again that only one of the indirect catalyzers is undergoing considerable changes of concentration, we have:

$$\frac{(a' + x)^{m'} (b' + x)^{n'} \ldots}{(a - x)^m (b - x)^n \ldots} \cdot \frac{z^{m + n + \ldots -1}}{z^{m' + n' + \ldots -1}} = \frac{k_0}{k'_0} \cdot \kappa - \kappa')S = K.$$

The principle here involved, that κ and κ' are not necessarily equal, and that, therefore, the ordinary equilibrium "constant" K of the mass law may vary with the concentration S of an indirect catalyzer, is contrary to the belief that thermodynamics require the influence of a catalyzer to be the same on both sides of a balanced reaction. As a matter of fact, this requirement only applies where the molecular state of the reagents is not affected by the catalyzer. In different solvents the equilibrium of one and the same reaction is well known to be different; and our

principle and equation of indirect catalysis are nothing else than the ordinary conception of solvent influence generalized and expressed mathematically.

If the equation here proposed is assumed to express generally the effect of indirect catalyzers, it furnishes important guidance in characterizing the type of catalysis involved in any given reaction and thus in deciphering the reaction mechanism itself. To mention a single example: we found that the retarding effect of water upon esterification follows the equation of indirect catalysis. From this we concluded that water, without itself taking part in the esterification, retards the reaction by its high dissociating power, and hence that esterification depends on the formation of complex molecules. This conclusion is in accord with a great deal of independent experimental evidence produced by several of my student-collaborators.

Further, having realized that the mechanism of a given reaction depends mainly on dissociation, or on the formation of complexes, as the case may be, one is enabled to foresee an indefinit number of substances that will act as positiv catalyzers and an indefinit number of other substances that will act as negativ catalyzers. Thus, having realized that esterification depends on the formation of complex molecules, we confidently expected that all substances of low dissociating power (and hence, presumably, high associating power) would greatly hasten that reaction. Experiment has strikingly confirmed this expectation in all cases tried.

These and similar practical services already rendered by the theory have encouraged me to bring it without further delay to the attention of other workers in chemical dynamics. A variety of experimental data supporting it will follow in a series of publications in course of the next few months.

WORCESTER, MASS.

AN IMPROVED APPARATUS FOR MEASURING THE CONDUCTIVITY OF ELECTROLYTES.

BY E. W. WASHBURN AND J. E. BELL.

1. Introduction.

As a preliminary to an investigation of the electrical conductivity of aqueous solutions of strong electrolytes in the concentration range included between 0.001 and 0.00001 normal, it became necessary to examin some of the sources of error inherent in the Kohlrausch method when applied to solutions of such high specific resistances. As a result of this study, an apparatus has been evolved which permits the *easy* attainment of a