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MEDIUM CHANGES IN HOMOGENEOUS CATALYSIS AND AN APPROACH TO THEIR THEORETICAL INTERPRETATIONBY HERBERT S. HARNED AND NICHOLAS N. T. SAMARAS¹

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The velocity of reaction between the substances A, B, etc., may be expressed by the equation

$$v = \bar{k}c_{ACB} \dots F \quad (1)$$

in which F is a kinetic factor which is a function of the concentrations c_A , c_B , etc., of some or all of the species present. \bar{k} is independent of the concentrations, and, consequently, the collision number, is but a function of the temperature.

From the thermodynamic requirements involving the reaction and its reverse, it has been proposed that the kinetic factor must contain the product of the activity coefficients, γ_A , γ_B , etc., of A, B, etc., as a consequence of which

$$v = \bar{k}'c_{ACB} \dots \gamma_A \gamma_B \dots F' \quad (2)$$

This equation will lead to a consistent thermodynamic result when F' is the same for the reaction as for its reverse at the time when the system approaches equilibrium. When F' equals unity, equation (2) expresses the activity rate theory.

A considerable advance in the interpretation of F has been made by Brönsted, who employs the equation²

$$v = \bar{k}'c_{ACB} \dots \frac{\gamma_A \gamma_B}{\gamma_{AB}} \dots F'' \quad (3)$$

where F'' is taken to be unity. γ_{AB} is the activity coefficient of a hypothetical intermediate complex. This equation has been particularly successful in accounting for positive and negative salt effects in dilute solutions, but does not provide a means of calculating even approximately the actual magnitude of the primary salt effect. In particular this is true in homogeneous catalysis which deals with reactions between ions and neutral molecules.

We shall define "the primary kinetic effect" as the influence of either salt addition or a solvent change upon F , and "the secondary kinetic effect" as the change in concentrations, c_A , c_B , etc., which may occur upon the addition of salts or solvents.

The present treatment of this subject departs somewhat from the point of view just outlined. We shall attempt a calculation of the primary

¹ This communication is a revised presentation of part of a thesis submitted by Nicholas N. T. Samaras to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

² Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1923); *Chem. Reviews*, **5**, No. 3 (1928).

and secondary kinetic effects from considerations involving electrostatics, and consider the relations of these deductions to thermodynamics.

Statistical Theory.—Christiansen³ has shown that in cases of reactions between two ions the velocity at constant temperature may be expressed by

$$v = \bar{k}'c_1c_2 e^{-\psi_1ez_2/kT} \quad (4)$$

where c_1 , c_2 are the concentrations of the two reacting ionic species, ψ_1 is the potential at a distance r from the first ion and z_2 is the valence of the second. Upon substituting for ψ_1 the value obtained for the potential of an ion from the limiting law of the theory of Debye and Hückel, Christiansen showed that for the case in question Brönsted's equation

$$v = \bar{k}'c_1c_2 \frac{\gamma_1\gamma_2}{\gamma_{12}} \quad (5)$$

follows. This equation has therefore a statistical basis and as before mentioned has been proved to be experimentally valid for reactions between ions in dilute solutions.

When, however, we are interested in a reaction involving an ion and a neutral molecule, this equation is not of great help, since in the region of concentration in which it may be expected to be valid, it leads simply to the classic law by reason of the fact that the primary factor, $\gamma_1\gamma_2/\gamma_{12}$, equals unity. Upon extending the theory somewhat, Brönsted showed that a linear salt effect may be expected. No attempt was made by him to compute this effect.

In the present study, we seek the principal cause of the variation of the reaction velocity of reactions between ions and neutral molecules with change in the character of the medium brought about by salt addition or by actual change of solvent. We shall endeavor to show that this change in cases where the catalyst remains the same may be computed by an equation of the form

$$\bar{k} = \bar{k}_0c e^{-W/kT} \quad (7)$$

where \bar{k} is the velocity constant in the medium in question, \bar{k}_0 the velocity constant in the original medium before the change was effected, c the concentration of catalyst and $e^{-W/kT}$ a Boltzmann factor. Stated in this manner, our problem resolves itself into ascertaining the character and magnitude of W from fundamental electrostatic considerations. We appreciate that owing to the complexity of the general problem we cannot hope to achieve a complete result, that is to say, to obtain an expression for W which is valid in all cases. On the other hand, we can obtain W for some cases and thereby show that one of the factors of greatest importance is known.

Electrostatic Theory and the Work Term Involved in Exchange of Solvent and Transfer of Ion.—The following preliminary treatment

³ Christiansen, *Z. physik. Chem.*, 113, 35 (1929).

(equations 8 to 15) is that employed by Butler⁴ in a contribution to the theory of the salting out effect, and is presented here in order to make clear the definitions of the quantities involved. The development after equation (15) is based upon a different conception than that of Butler and does not involve certain numerical approximations made by him.

If a molecule of volume δv is brought from an infinite distance where the electrostatic field is zero to a distance r from an ion of charge $z_1 e$ (e is electronic charge, z_1 the valence of ion) at which position the field is E , then the work done by the electric field is given by the expression

$$\delta v \int_0^E P dE \quad (8)^5$$

Since P is the polarization per unit produced by the field, it is proportional to it, so that

$$P = \alpha E \quad (9)$$

where the proportionality factor is the susceptibility and is a constant for isotropic media.⁶ α is related to the dielectric constant, D , by the equation

$$D = 1 + 4\pi\alpha \quad (10)$$

From equations (8) and (9), the work produced by bringing δv_{II} from ∞ to r is

$$\delta v_{II} \int_0^E \alpha_{II} E dE = \alpha_{II} \delta v_{II} \frac{E^2}{2} \quad (11)$$

Now, if the ion is in solvent I, and δv_{II} of solvent II is brought to a distance r from it, an equal volume of solvent I must be displaced, and the work done against the electric forces in removing this molecule will be

$$\delta v_{II} \int_0^E \alpha_I E dE = \alpha_I \delta v_{II} \frac{E^2}{2} \quad (12)$$

Therefore the work done against the electric forces in accomplishing the exchange will be given by

$$(\alpha_I - \alpha_{II}) \delta v_{II} \frac{E^2}{2} \quad (13)$$

The potential, ψ , at a distance r from the ion is ez_i/Dr , and the field is given by

$$E = \frac{\partial \psi}{\partial r} = -\frac{ez_i}{Dr^2} \quad (14)$$

As a result the work term, dW , for this exchange of element of volume, δv_{II} , is

$$dW = (\alpha_I - \alpha_{II}) \delta v_{II} \frac{e^2 z_i^2}{2D^2 r^4} \quad (15)$$

⁴ Butler, *J. Phys. Chem.*, **33**, 1015 (1929).

⁵ Livens, "Theory of Electricity," Chapt. 5, Cambridge University Press, 1918.

⁶ Page, "Introduction to Theoretical Physics," D. Van Nostrand Co., New York, 1928, pp. 325-336.

dW in equation (15) may be regarded as the work done against the electric forces necessary to change the dielectric constant of the medium at a distance r from the ion by an amount equal to

$$(\alpha_I - \alpha_{II}) \delta v_{II} = \frac{(D_I - D_{II})}{4\pi} \delta v_{II} \quad (16)$$

where D_I and D_{II} are the dielectric constants of solvent I and substance II, respectively. Consequently, if (15) be integrated over the entire volume, we shall obtain the work necessary to change the dielectric constant of the whole medium by that same amount. Therefore

$$dW = \int_{r=a_i}^{\infty} (\alpha_I - \alpha_{II}) \delta v_{II} \frac{e^2 z_i^2}{2D_I r^4} 4\pi r^2 dr \quad (17)$$

or

$$dW = \frac{e^2 z_i^2}{2D_I^2 a_i} 4\pi (\alpha_I - \alpha_{II}) \delta v_{II} \quad (18)$$

where a_i is the ionic radius. In integrating D has been assumed to be constant. This is entirely justifiable since the over-all change in dielectric constant is of the order of an infinitesimal.

If n_{II} is the number of molecules of kind II per cc., the total change in dielectric constant will be

$$4\pi (\alpha_I - \alpha_{II}) \delta v_{II} n_{II} = (D_I - D_{II}) \delta v_{II} n_{II} = D - D \quad (19)$$

where D is the dielectric constant of the solution. The total work in bringing about this change is given by the expression

$$W = \frac{e^2 z_i^2}{2a_i} 4\pi (\alpha_I - \alpha_{II}) \delta v_{II} \int_0^{n_{II}} \frac{dn_{II}}{D^2} \quad (20)$$

if the substance is brought up bit by bit in a medium of varying dielectric constant D .

This equation may be integrated since as a first approximation we may represent D as a linear function of n_{II} , or $D = D_I - Bn$, where B is a constant, and n is the number of moles per cc. Equation 20 becomes

$$\begin{aligned} W &= \frac{e^2 z_i^2}{2a_i} 4\pi (\alpha_I - \alpha_{II}) \delta v_{II} N \int_0^n \frac{dn}{(D_I - Bn)^2} \\ &= \frac{e^2 z_i^2}{2a_i} 4\pi (\alpha_I - \alpha_{II}) \delta v_{II} \frac{N}{B} \left(\frac{1}{D_I - Bn} - \frac{1}{D_I} \right) \\ &= \frac{e^2 z_i^2}{2a_i} 4\pi (\alpha_I - \alpha_{II}) \delta v_{II} \frac{N}{B} \left(\frac{1}{D} - \frac{1}{D_I} \right) \end{aligned} \quad (21)$$

upon introducing these relations if N is Avogadro's number. From (16), $4\pi (\alpha_I - \alpha_{II}) = D_I - D_{II}$, where D_I and D_{II} are the dielectric constants of the pure substances I and II, respectively. Further, $\delta v_{II} N$ equals the molecular volume, M/d , and B equals $(D_I - D_{II})/n'_{II}$ where n'_{II} is the number of moles of pure substance II in 1 cc., or $n'_{II} = d/M$. Hence $B = [(D_I - D_{II})/d]M$. Upon substitution of these relations in (21), we obtain

$$W = \frac{e^2 z_i^2}{2a_i} (D_I - D_{II}) \frac{M}{d} \frac{d}{M(D_I - D_{II})} \left(\frac{1}{D} - \frac{1}{D_I} \right) = \frac{e^2 z_i^2}{2a_i} \left(\frac{D_I - D}{DD_I} \right) \quad (22)$$

The same equation may be obtained more simply if not so rigorously from equation (18), if we regard $4\pi(\alpha_I - \alpha_{II})\delta v_{II}$ to represent an infinitesimal lowering of dielectric constant, $-dD$, produced by one molecule of volume δv_{II} . If this is constant, the lowering of the dielectric constant is a linear function of the number of moles, n . Therefore

$$W = \frac{e^2 z_1^2}{2a_1} \int_{D_1}^D - \frac{dD}{D^2} = \frac{e^2 z_1^2}{2a_1} \left(\frac{1}{D} - \frac{1}{D_1} \right) \quad (22)$$

We have calculated the work against the electric forces corresponding to bringing a volume $n_{II}\delta v_{II}$ of n_{II} molecules of substance II into the solution which replace an equal volume of solvent I. This is identical but opposite in sign with the work done by the electric forces, W_e , when the ion is transferred from solvent I to a solution containing n molecules of substance II. Therefore, according to thermodynamics

$$-W_e = \Delta \bar{F} = kT \ln \frac{\gamma}{\gamma_I} = \frac{e^2 z_1^2}{2a_1} \frac{4\pi(\alpha_I - \alpha_{II})\delta v_{II} n_{II}}{DD_1} \quad (23)$$

where γ and γ_I are the activity coefficients of the ion in the solution and pure solvent I, respectively, and $\Delta \bar{F}$ is the partial free energy of transfer.⁷ From the latter point of view, equation (22) is seen to be that developed by Born⁸ from considerations involving ion transfer. The above deduction is more detailed from an electrostatic point of view than that of Born, and throws further light upon the mechanism of the medium changes.

In some of the following calculations, it is numerically simpler and sufficiently accurate to put DD_1 in (23) equal to D_1^2 . Upon this basis it is clear that (23) becomes

$$-W_e = \frac{e^2 z_1^2}{2a_1 D_1^2} 4\pi(\alpha_I - \alpha_{II})\delta v_{II} n_{II} = \frac{e^2 z_1^2}{2a_1 D_1^2} (D_1 - D) = kT \ln \frac{\gamma}{\gamma_I} \quad (24)$$

This latter expression will be found very useful and simple for computing many of the results.

Returning now to the theory of homogeneous catalysis, if we consider a reaction to take place between a neutral molecule and an ion, we obtain from equations (1) and (2)

$$\bar{k} = \bar{k}_0 m_h \gamma_n \gamma_i F' = \bar{k}_0 m_h F \quad (25)$$

Further, from equation (23), we found that the effect of the medium upon the activity coefficient of one species is given by

$$\frac{\gamma}{\gamma_I} = e^{-W_e/kT}$$

Since F is a function of the " γ 's," this latter equation and equation (25) permit us to write equation (7) in the more definite form

$$\bar{k} = \bar{k}_0 m_h e^{-nW_e/kT} \quad (26)$$

⁷ We speak of individual ion activity coefficients at this time. In applying this equation, activity coefficient products and ratios should probably be employed.

⁸ Born, *Z. Physik*, 1, 45 (1920).

where W_e is defined by (23), and n is an integer depending upon the number of species involved. If we anticipate our examination of the data of many reactions, we find that n is usually 1, although we have found a case where it appears to be -1 . Sometimes W_e is very small so that n appears to be zero.

Calculation of the Secondary Kinetic Effect Caused by Change of Medium upon the Velocity of Hydrolysis of Ethyl Orthoformate.—The hydrolysis of ethyl orthoformate is so sensitive to hydrogen ions that buffered solutions such as acetic acid–sodium acetate mixtures must be employed. Consequently, there will be a secondary medium effect due to the decrease in the concentration of the hydrogen ion produced by the change of medium. Since for acetic acid in any medium at constant temperature and pressure, the thermodynamic equilibrium condition is expressed by $K = (\gamma_H \gamma_{AC} / \gamma_{HAC}) (m_H m_{AC} / m_{HAC})$, and since m_{AC} / m_{HAC} is a constant in the case of the solutions under consideration, we find that in the two media the hydrogen-ion concentration ratio is given by

$$\frac{m_{H_1}}{m_H} = \frac{\gamma_H \gamma_{AC} \gamma_{HAC_1}}{\gamma_{H_1} \gamma_{AC_1} \gamma_{HAC}} = \frac{\gamma_H \gamma_{AC}}{\gamma_{H_1} \gamma_{AC_1}} \quad (27)$$

if we neglect the small change in the activity coefficient of the undissociated molecule produced by the molecular, not the ionic, fields. Since the velocity constant due to this secondary effect is proportional to the hydron concentration, $\frac{\bar{k}_0}{\bar{k}} = m_{H_1} / m_H$, and consequently from equations (24) and (27)

$$\ln \bar{k}_0 - \ln \bar{k} = \ln m_{H_1} - \ln m_H = \frac{e^2}{D_1^2 a_i k T} (D_1 - D) = \frac{-2W_e}{kT} \quad (28)$$

Substituting 4.77×10^{-10} e. s. u., 78.8, 1.37×10^{-16} ergs for e , D_1 and k , respectively, and employing 1.5 Å. as a probable value for the mean value of the hydrogen and acetate ions, we obtain

$$\ln \bar{k}_0 - \ln \bar{k} = 0.06(D_1 - D) \quad (29)$$

Harned and Samaras⁹ have shown that in the case of seven solvents the experimental results yield

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07(D_1 - D) \quad (29a)$$

For simplicity, the approximate equation (24) has been employed. If the more exact equation (23) had been used

$$\ln \bar{k}_0 - \ln \bar{k} = \frac{0.06 D_1^2}{D D_1} (D_1 - D) \quad (29b)$$

would have been obtained. For the data in question, and owing to the uncertainty involved in the assigned value of a_i , (29) is as numerically valid as (29b).

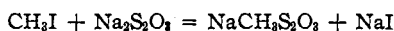
Thus we may interpret the data by a secondary medium effect which in terms of the velocity constant is expressed by

$$\bar{k} = \bar{k}_0 e^{2W_e/kT}$$

⁹ Harned and Samaras, THIS JOURNAL, 54, 1 (1932).

On the other hand, this computation does not exclude a primary medium effect. Although we believe the factor of greatest importance and magnitude has been computed, we cannot in view of the lack of data determine how or whether the kinetic factor, F , varies with the changing character of the medium. Our result indicates a small primary effect. This is substantiated by the data of Manning,¹⁰ who found that dextrose had no effect on the velocity of hydrolysis of ethyl formate, and by Robinson,¹¹ who showed that 1.68 M dextrose had no appreciable effect on the velocity of hydrolysis of ethyl acetate when catalyzed by 0.1 M hydrochloric acid.

A Calculation of Two Primary Medium Effects.—Prasad and Godbole¹² have measured the velocity constant of the reaction,



in mixtures of water and methyl, ethyl, isopropyl and n -propyl alcohols. The plots of $\log \bar{k}$ against the weight per cent. of alcohol are straight lines, using the extrapolated $\log \bar{k}_0$ values, up to concentration of 10, 20, 30 and 60%, for the solutions of n -propyl, isopropyl, ethyl and methyl alcohols, respectively. Above these concentrations, there is a sharp decrease in $\log \bar{k}$ which these investigators ascribed to compound formation. In Table I are given the results read from plots of their data which show the increase in velocity caused by the addition of 20% of the alcohols in question.

TABLE I
SHOWING COMPUTATION OF EXPERIMENTAL CONSTANT OF EQUATION 30

Alcohol	$\ln \bar{k} - \ln \bar{k}_0$	$D_I - D$	$\frac{\ln \bar{k} - \ln \bar{k}_0}{D_I - D}$
Methyl (20%)	0.47	9.8	0.05
Ethyl (20%)	.68	11.9	.06
Isopropyl (20%)	.80	13.2	.06
n -Propyl (20%)	.83	13.9	.06

The column headings are self-explanatory. The experimental results lead to

$$\ln \bar{k} - \ln \bar{k}_0 = 0.06(D_I - D)$$

which is in accord with the primary factor in equation (26) when n equals +1, and where W_e is given by equation (25). For monovalent ions, $W_e/kT = 0.03(D - D_I)$, but in the case of a univalent salt, $-W_e/kT = 0.06(D_I - D)$, if a_i is taken to be 1.5 Å. The valence factor is $\Sigma z_i^2/\nu$ where ν is the number of ions formed from one molecule of electrolyte. Thus, the kinetic factor is given by $e^{-W_e/kT}$.

¹⁰ Manning, *J. Chem. Soc.*, **119**, 2079 (1921).

¹¹ Robinson, *Trans. Faraday Soc.*, **26**, 217 (1930).

¹² Prasad and Godbole, *J. Ind. Chem. Soc.*, **7**, 127 (1930).

¹³ For sources of dielectric constant lowerings, see Harned and Samaras, *THIS JOURNAL*, **54**, 1 (1932).

The above agreement should be considered as qualitative rather than quantitative because of the insufficient number of points given by the investigators, and also because the extrapolated zero value and not the experimental one was used in deriving the values shown in Table I.

From a quantitative viewpoint the thorough investigations of Fontein^{13a} on the transformation of acetylchloroaminobenzene and related compounds by 0.2 *N* hydrochloric acid in water-alcohol mixtures are of great interest as a test of equation (26). When the $\log \bar{k} - \log \bar{k}_0$ values for the transformation of acetylchloroaminobenzene in water-methyl alcohol solutions are plotted against $(1/D - 1/D_1)$, a straight line is obtained for all the mixtures with a slope equal to 174; the methyl alcohol concentration is as high as 83.3 weight per cent. The velocity constants of the transformations of formylchloroaminobenzene, acetylchloroaminobenzene, propionylchloroaminobenzene, butyrylchloroaminobenzene, benzoylchloroaminobenzene, acetylchloroamino-*m*-methylbenzene and acetylchloroamino-*m*-chlorobenzene have been determined in water-ethyl alcohol mixtures. The $\log \bar{k} - \log \bar{k}_0$ values for a given alcohol concentration were found to be practically the same and were therefore averaged for all seven substances and the mean values plotted against $(1/D - 1/D_1)$; the slope of the resulting straight line is 142. Thus we have

$$\ln \bar{k} - \ln \bar{k}_0 = 327 \left(\frac{1}{D} - \frac{1}{D_1} \right)$$

From equations (26) and (23), taking again $n = 1$

$$\ln \bar{k} - \ln \bar{k}_0 = \frac{\epsilon^2}{2akT} \left(\frac{1}{D} - \frac{1}{D_1} \right) = 330 \left(\frac{1}{D} - \frac{1}{D_1} \right)$$

For hydrochloric acid the value of a , which is defined by

$$\frac{1}{a} = \frac{1}{2} \left[\frac{1}{a_{H^+}} + \frac{1}{a_{Cl^-}} \right]$$

is 0.85×10^{-8} from the values of ionic radii given by Bragg and Pauling.^{13b}

The agreement between the theoretical and experimental slopes leaves little to be desired in the case of water-ethyl alcohol mixtures; for the transformation of acetylchloroaminobenzene in water-methyl alcohol solutions the experimental slope is high, being 400.

A Calculation of a Primary Salt Effect.—We shall now consider the iodide-ion catalysis of hydrogen peroxide, and compute the primary medium effect produced by salt addition. To do this, we shall employ the same considerations and assume that the salt effect is a function of the change in dielectric constant of the medium just as in the previous cases where the influence of the change in medium upon the reaction velocity has been shown to be a function of a measured change in dielectric constant.

^{13a} Fontein, *Rev. Trav. Chim.*, **47**, 635 (1928).

^{13b} Bragg, *Phil. Mag.*, [6] **40**, 169 (1920); Pauling, *THIS JOURNAL*, **49**, 765 (1927).

It is well known that the measured activity coefficients, γ , of an electrolyte may be represented by Hückel's equation,¹⁴ or

$$\log \gamma = - \frac{u \sqrt{\Gamma}}{1 + A \sqrt{\Gamma}} + B\Gamma - \log(1 + 0.018 \nu m) \quad (30)$$

u is the universal constant of the Debye and Hückel theory, A allows for the sizes of the ions, and from it the mean distance of approach of ions may be computed. The logarithmic term on the right allows for the purely formal relation between the activity coefficient, f , defined by a/N where a is the activity and N is the mole fraction and γ , or a/m where m is the molality. Further, Γ equals $\sum c_i z_i^2$, where c_i is the concentration of an ion in moles per liter of solution and the summation is for all the ions. B was assumed by Hückel to be caused by the change in dielectric constant of the medium brought about by the addition of the electrolyte. Hückel assumes that this variation is linear according to the law, $D_0 - D = \sum \delta_i c_i$, where δ_i is a constant characteristic of an ion and the summation is for all the ions. Hückel obtains his value for B by computing the effect of change in dielectric constant upon the charging process of the ion and subsequently the related influence upon the activity coefficient. This method leads to a linear variation of the logarithm of γ which agrees with the observed results but, as pointed out by Harned,¹⁵ the predicted lowering of the dielectric constant is much too great, in fact so great that the dielectric constant would become negative in some electrolytic solutions at 4 M concentration.

By considerations which involve the salting out effect of ions, Butler obtained

$$\ln f_{12} = \frac{e^2}{2kTD^2} \frac{4\pi(\alpha_1 - \alpha) \delta v N}{1000 \times a} \Gamma = 2.3 B\Gamma \quad (31)$$

f_{12} is that part of the activity coefficient which is caused by the fact that the solvent molecules because of their polar nature congregate around an ion, thereby displacing or "salting out" other ions; a is the mean ionic radius, α is the average value of the susceptibility of the ions of the salt, α_1 the susceptibility of water, so that $4\pi(\alpha_1 - \alpha) \delta v$ is the average lowering of the dielectric constant produced by one ion per cc. Therefore

$$\frac{4\pi(\alpha_1 - \alpha) \delta v N}{1000} \sum m_i = D_1 - D \quad (32)$$

or the total lowering of the dielectric constant.

Equation 23 was obtained from the process of bringing a molecule of substance II up to the ion and replacing a molecule of substance I. Similarly, we can bring the ions of a salt to the neighborhood of an ion and replace the solvent, and an equation will be obtained identical with (23) with the exception that we must now use mean values. If this is done we

¹⁴ Hückel, *Physik. Z.*, 25, 93 (1925).

¹⁵ Harned, *THIS JOURNAL*, 48, 326 (1926).

may readily obtain from (23) the following expression for W_e (for a binary electrolyte)

$$-\frac{W_e}{kT} = \frac{z_+z_- e^2 (D_1 - D)}{2akT} = \frac{4\pi (\alpha_1 - \alpha) \delta v N e^2}{2akT DD_1 1000} \Gamma = 2.3 B\Gamma \quad (33)$$

which is identical with (31) except that we have DD_1 in the denominator instead of D^2 . W_e is to be interpreted as the work done by the electrical forces in bringing up from an infinite distance the salt, ion by ion, to a distance a from an ion until the dielectric constant is D , or, more simply, $-W_e$ may be looked upon as the electrical energy gained by transfer of an ion from a medium of dielectric D_1 to one of D .

According to the theory, since there is no secondary salt effect, the kinetic factor is given by $e^{-W_e/kT}$ and the velocity constant by $\bar{k} = \bar{k}_0 e^{-W_e/kT}$ [using (26) and taking n equal to 1], where \bar{k}_0 is the velocity constant in the solution before the salt addition. Thus we find from equations (26) and (33) that

$$\begin{aligned} \ln \bar{k} - \ln \bar{k}_0 &= 2.3 B\Gamma \text{ or} \\ \log \bar{k} - \log \bar{k}_0 &= B\Gamma \end{aligned} \quad (34)$$

It has already been pointed out by French,¹⁶ and by Harned and Åkerlöf¹⁷ in previous discussions of the iodide ion catalysis of hydrogen peroxide that the neutral salt effects follow the order of the B constants. That equation (34) is valid is shown clearly in Table II. $\log \bar{k} - \log \bar{k}_0$ was plotted for each salt against the concentration of salt. The slopes were determined for each of the salts listed and are given in the second column. The third column contains $B\Gamma/c$, where the B values were obtained from electromotive force measurements of the activity coefficients.¹⁸

TABLE II
VERIFICATION OF EQUATION 34

Salt	$\frac{\log \bar{k} - \log \bar{k}_0}{c}$	$\frac{B\Gamma}{c} = 2B$
NaBr	0.080	0.080
KBr	.036	.040
KCl	.028	.034
NaCl	.062	.064
LiCl	.139	.140
		$\frac{B\Gamma}{c} = 6B$
K ₂ SO ₄	-0.019	-0.094
Na ₂ SO ₄	.020	-.030
Li ₂ SO ₄	.074	.052
BaCl ₂	.29	.23
SrCl ₂	.26	.29

¹⁶ French, *J. Phys. Chem.*, **32**, 401 (1928).

¹⁷ Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1928).

¹⁸ Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926). Harned, *THIS JOURNAL*, **51**, 416 (1929).

The agreement between the theory and the experimentally derived results is excellent for the uni-univalent salts. For the univalent salts it is not so good, but it should be observed that any error in B is multiplied by 6, and in these cases the B constants are not as well known. Further, we observe that the order of the results is correct for the sulfates, and that potassium sulfate with a negative B constant decreases the velocity.¹⁹

It is seen from equations (33) and (34) that the experimental results show that the velocity constant depends upon the dielectric constant lowerings produced by the ions of the various salts; in other words, the velocity constant is a function of the transfer of ions and not the neutral hydrogen peroxide molecule. If we consider homogeneous catalysis, in general, it is not only conceivable but probable that in many cases it will be necessary to take into account the transfer of the neutral substrate molecule if this condition be required by the mechanism of the reaction. The activity coefficient of the neutral molecule in the salt solution, as given by Butler, is

$$\ln \gamma_B = \frac{4\pi (\alpha_I - \alpha_B) \delta v_B e^2 N}{2kT D^2 1000} \sum \frac{m_i z_i^2}{a} = - \frac{W'_0}{kT} \quad (35)$$

This equation is identical with that of Debye and MacAulay²⁰ with the exception that D^2 and not D_I^2 appears in the denominator. Our treatment would lead to DD_I . It is apparent that $\ln \gamma_B$ depends on $(\alpha_I - \alpha_B)$, the concentration of ions, and the values of a_i of the salts. Thus, if the susceptibility of the reacting substance is the same as that of water, γ_B does not change upon salt addition. In the reaction under consideration any change in γ_B is small since the dielectric constant of a solution of 45% hydrogen peroxide is only 2.5% higher than water. Therefore in the iodide-ion catalysis of hydrogen peroxide this complicating factor does not enter to an appreciable extent, a conclusion which may account for the validity of equation (34).

Although we cannot be expected to achieve exact results with a theory as approximate as the one we have used, we have obtained valuable support of the contention that the linear salt effect and the linear kinetic salt effect are both functions of the change in dielectric constant of the medium produced by salt addition, since we have employed the same theory for both salt effects and medium effects involving known changes in the dielectric constant.

Before we leave the discussion of the iodide-ion catalysis of hydrogen peroxide, we shall point out an interesting fact which so far we have been

¹⁹ The correction of the first member on the right of equation (30) due to the development of the Debye and Hückel theory by Gronwall, La Mer and Sandved [*Physik. Z.*, **29**, 358 (1928)] in the case of bivalent electrolytes will unquestionably alter the B -values.

²⁰ Debye and MacAulay, *ibid.*, **26**, 22 (1925).

unable to explain. Bohnsen²¹ has determined the velocity constants of this reaction in water and in mixtures of water with glycerin, ethyl and methyl alcohols. Up to concentrations of 30% of these compounds $\ln \bar{k} - \ln \bar{k}_0$ equals a constant times the molality of the organic solvent. In Table III are given the values of $\ln \bar{k} - \ln \bar{k}_0$, $D_0 - D$ at 20 wt. % organic solvent concentration, and the slope of the plot of $\ln \bar{k} - \ln \bar{k}_0$ against $D_0 - D$.

TABLE III
CONSTANTS OF EQUATION 30 FOR THE IODIDE-ION CATALYSIS OF HYDROGEN PEROXIDE IN ORGANIC SOLVENTS

Solvent	$\ln \bar{k} - \ln \bar{k}_0$	$D_0 - D$	$\frac{\ln \bar{k} - \ln \bar{k}_0}{D_0 - D}$
Methyl alcohol (20%)	-0.471	9.8	-0.048
Ethyl alcohol (20%)	- .530	12.0	- .044
Glycerin (20%)	.223	4.4 ^a	.051

^a Estimated from audio frequency.

Although the numerical values are of the expected order of magnitude, there is a decrease of reaction velocity in the case of the alcohols and an increase in glycerin solutions. We can merely state this result without further explanation by equation (26), where n is +1 for glycerin solutions and -1 for methyl and ethyl alcohol solutions if a_i is taken to be 1 Å., and n is +2 or -2, respectively, if a_i is 2 Å.

The Relation of the Simple Theory to the More Complicated Cases of Homogeneous Catalysis.—We have now to consider briefly two examples of homogeneous catalysis which cannot be computed by the theory in its simple form and for the present we shall limit the discussion to showing that in these cases the difficulties reside in the computation of W in equation (7), in other words, our simple calculation of W_e and W'_e does not suffice.

From the data on the neutral salt catalysis of ethyl acetate, Harned and Åkerlöf²² have pointed out and Robinson has verified with eleven salts that the velocity constant, \bar{k}_0 , of hydrolysis of ethyl acetate with 0.1 N hydrochloric acid in salt solutions is related to that, \bar{k}_0 , in the 0.1 N hydrochloric acid solution by the equation

$$\bar{k} = \bar{k}_0 \gamma_e^{1/2} \quad (36)$$

where γ_e is the activity coefficient of the ester as determined from solubility measurements. Thus

$$\ln \bar{k} - \ln \bar{k}_0 = \frac{1}{2} \ln \gamma_e = -\frac{1}{2} \frac{W'_e}{kT}$$

or

$$\bar{k} = \bar{k}_0 e^{-1/2 W'_e / kT} \quad (37)$$

²¹ Bohnsen, *J. Phys. Chem.*, **24**, 677 (1920).

²² Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1928); Robinson, *ibid.*, **26**, 127 (1930).

In this case, however, γ_e may not be computed completely for the salts in question by the Debye and MacAuley equation or equation (35). For example, γ_e in lithium iodide solutions is less than in water, a result which is entirely in disagreement with the calculation. In this case the fault lies in the fact that all the required factors have not been employed in the calculation of W'_e in equation (35).

The hydroxyl-ion catalysis of decomposition of diacetone alcohol, which has been studied very comprehensively by Åkerlöf, offers quite a different and even more interesting case which we are unable to calculate by the simple theory. Åkerlöf²³ showed that, in general, the velocity constant changes caused by changes of concentration of the hydroxide catalysts as well as the addition of various salts to the catalysts at constant concentration paralleled the behavior of the activity coefficients of the hydroxides.²⁴ Consequently, we have evidence that W in the kinetic factor in equation (7) is to a large extent a function of the transfer of the ions of the hydroxides. The actual calculation of this work term has not been made since it involves further considerations than those yet employed in the computation of W_e . The unmodified theory is unable to account for the peculiarities of the solutions containing the hydroxyl ion.²⁵

A consideration of the effect of change of medium upon the hydroxide-ion catalysis of diacetone alcohol indicates one additional factor. In Fig. 1,

²³ Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); **49**, 2955 (1927); **50**, 1272 (1928); **51**, 984 (1929).

²⁴ Harned and Åkerlöf, *Trans. Faraday Soc.*, **29**, 666 (1928).

²⁵ Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Harned, Chap. XII in Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1930.

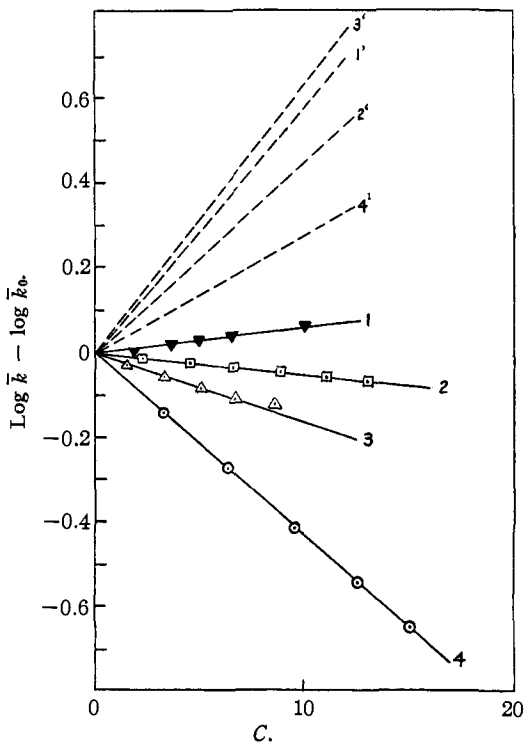


Fig. 1.—Theoretical and observed $\log \bar{k} - \log \bar{k}_0 - C$ plots for the decomposition of diacetone alcohol in water-alcohol mixtures: 1-1', isopropyl; 2-2', ethyl; 3-3', *n*-propyl; 4-4', methyl.

$\log \bar{k} - \log k_0$ in mixtures of water and some alcohols has been plotted against C , the concentration of alcohol in moles per 1000 g. of solution and is represented by the full lines. It is important to note that in all cases the plots are straight lines to concentrations as high as 50 wt. % alcohol, and for methyl alcohol up to 100%. The theoretical results computed from the equation, $\ln \bar{k} - \ln k_0 = -W_e/kT$, where W_e is derived from equation (24), are represented by the dashed lines. We see that the order is the same with the exception of that of *n*-propyl alcohol. The additional factor which may account for the observed decreases rather than the predicted increases of \bar{k} is possibly the formation of alcoholate ions of lower catalytic activity than the hydroxyl ion.

In conclusion, the empirical relation proposed by Grube and Schmid,²⁶ $\bar{k} = k_0 \times 10^{rc}$, for the effect of neutral salts upon the velocity constant of hydrolytic reactions, should be mentioned. Since r and C are a specific constant and the normal concentration of the salt, respectively, it is obvious that this expression is similar to our equations by means of which we have attempted to evaluate r in some cases.

More recently Gross²⁷ concluded that at least in some reactions between an ion and a neutral body, γ_A/γ_{AB} in equation (3) is unity, and derived an expression for the activity coefficient of the neutral substance, γ_B , in a salt solution. It may be easily shown that his expression for γ_B can be obtained from (13) by Butler's procedure, if the total Debye and Hückel potential, which involves both the potential due to the ion itself and that due to the interionic forces, instead of the ion potential alone is used. These more complicated aspects of the problem will be taken up in a further communication.

Summary

1. In this study we have attempted to express the kinetic factor, F , for medium effects in homogeneous catalysis by $e^{-W/kT}$ and have sought a value of W which is consistent with electrostatics and the experimental results. For examples in which complicating factors such as change of catalyzing ion, etc., are avoided, we have found that W may be represented with a fair degree of approximation by equations (23) or (24), and (33). This work term is associated with the dielectric constant change produced by a neutral substance or a salt.

2. The secondary medium effect of the hydrolysis of ethyl orthoformate catalyzed by acetic acid-sodium acetate buffer solutions has been successfully computed.

3. The primary medium effect of the reaction between methyl iodide and sodium thiosulfate and the transformations of substituted chloroaminobenzenes are in agreement with the theory.

²⁶ Grube and Schmid, *Z. physik. Chem.*, 119, 19 (1926).

²⁷ Gross, *Monatsh.*, 53-54, 445 (1929).

4. The primary salt effect upon the iodide-ion catalysis of hydrogen peroxide agrees remarkably well with the theoretical prediction.

5. The hydrogen-ion catalysis of ethyl acetate and the hydroxide-ion catalysis of decomposition of diacetone alcohol are too complicated to be computed by the simple theory. It is shown, however, that this is due to complicating factors involved in the calculation of W .

6. We are quite aware of the many difficulties confronting further advances in the interpretation of this complicated situation and realize that the simple theory is but an approximation. On the other hand, we believe that the factor of greatest importance is known.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE THERMAL DECOMPOSITION OF AMMONIA ON THE SURFACE OF OSMIUM

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While there have been many kinetic investigations of catalytic reactions in recent years, it cannot yet be said that there is universal agreement as to the precise function of the catalyst. For a surface reaction, the most likely major action of the catalyst is to lower the energy of activation¹ as compared with the requirement for the corresponding homogeneous reaction, since this is the dominant rate controlling factor for homogeneous reactions.² This action of a catalyst would be more evident were it not for the adsorption of products in some cases, which may have the effect of increasing the apparent energy of activation.³ This action of reaction products may go so far as to crowd the reactant almost completely off the surface and defeat the action of a catalyst which might lower the activation energy requirement to a degree sufficient for rapid reaction.

Thus, in addition to lowering the energy of activation, an effective catalyst must also preserve a suitable adsorption balance between reactants and products.

Osmium was found by Haber and Le Rossignol⁴ to be a very effective catalyst for the synthesis of ammonia, and therefore for its decomposition. We have found that the catalyst with a suitable preliminary treatment assumes a constant activity. The thermal decomposition of ammonia on

¹ Sixth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **32**, 1601 (1928).

² "Material chains" would require further elaboration of this generalization.

³ Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," 1929, 2d ed., p. 234.

⁴ Haber and Le Rossignol, *Z. Elektrochem.*, **19**, 53 (1913).