of alcohol when starting from the ether side. The equilibrium value of 15.0 mole % of alcohol lies between the two as it should. At 275°, the recovered liquid contained 73.5 mole % of alcohol when starting from the alcohol side and 8.5 mole % when starting from the ether side, these values being on either side of the equilibrium value of 38.0 mole % as they should be.

So far as the writers are aware, these experiments constitute the first preparation of alcohol from ether and water on a laboratory scale.

Summary

The position of equilibrium in the reaction, $2C_2H_5OH_{(v)} \rightleftarrows (C_2H_5)_2O_{(v)} + H_2O_{(v)}$ has been determined at 275°, using alumina as catalyst, and at 130°, using a sulfuric acid-alcohol mixture as catalyst. The values of the equilibrium constants are 0.66 and 8.0, respectively. These correspond to maximum possible conversions of alcohol to ether of 62.0% at 275° and 85.0% at 130°.

The free-energy change in the reaction and the free energy of formation of ether vapor at 25° have been calculated and found to be, respectively, —3210 cal. and —35,900 cal.

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THE RELATION BETWEEN THE TEMPERATURE COEFFICIENT AND THE MECHANISM OF A CHEMICAL REACTION

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A great number of reactions between dissolved substances are characterized by the fact that they proceed at a slow, measurable rate; in the field of inorganic chemistry, reactions between dissolved substances usually proceed at a rate too fast to be measured, although occasionally we find a slow reaction such as the catalytic decomposition of hydrogen peroxide by the iodide ion; on the other hand, in the field of organic chemistry, reactions between dissolved substances usually proceed at a measurable rate. A striking characteristic of these slow reactions is that in nearly all cases they are catalytic; indeed, the few exceptions to this may prove ultimately to be catalytic, so that the study of reaction velocity may be said to be a study of catalysis.

By assuming that reaction rate is proportional to the concentrations of reactants, a satisfactory formulation of experimental results has been obtained in practically all of the hundreds of reactions studied; when, however, we consider the variation of the rate with temperature we find that almost without exception, a rise in temperature of 10° increases the rate 200–400%; this is far above anything that can be accounted for on a simple kinetic basis.

Before considering the explanations of this anomaly it would be well to formulate some empirical generalizations that can be made from previous measurements of temperature coefficients. The first generalization is that reactions fall into comparatively few classes, each having a characteristic temperature coefficient; the hydrolysis by dil. hydrochloric acid in aqueous solution of all fatty acid esters,[1] β-substituted halogen fatty acid esters,[2] ethyl cyano-acetate and its homologs,[3] ethyl glycollate and its homologs[4] and formyl acetic acid[5] all have the same temperature coefficient $k_{35}/k_{25} = 2.4$ within experimental error. Evidently temperature coefficients are largely independent of the substrate, a conclusion that will be discussed more fully in a later section.

The second generalization is that the temperature coefficient of a reaction depends on the nature of the catalyst present; whereas changing the substrate is often without effect, changing the catalyst invariably changes the temperature coefficient. The hydrolysis by aqueous sodium hydroxide of ethyl acetate[6] and a number of hydroxy and alkyloxy fatty acid esters[7] gives $k_{35}/k_{25} = 1.8$ as compared with 2.4 for the corresponding hydrolysis by hydrochloric acid; the reaction between acetone and iodine catalyzed by hydrochloric acid gives $k_{35}/k_{25} = 3.0816$ as compared with 2.880 when catalyzed by sulfuric acid and 2.554 when catalyzed by sulfuric acid in the presence of 1.7 *M* ammonium sulfate solution. A solution of chlorine in benzene does not react in the dark,[8] unless catalyzed by certain substance such as iodine chloride, stannic chloride or ferric chloride; the temperature coefficients k_{35}/k_{25} for the reaction when catalyzed by these substances are 1.05, 1.5 and 2.5, respectively. Many additional examples might be given of the effect of change of catalyst on the temperature coefficient.

The third generalization is that the temperature coefficient of a reaction is independent of influences which greatly change the character of the solvent. Neutral salts have no effect on the temperature coefficient when a reaction is catalyzed by a strong acid; the value of k_{25}/k_0 for the hydrolysis

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[1] Ostwald, *J. prakt. Chem.*, **28**, 449 (1883). De Hemptinne, *Z. physik. Chem.*, **13**, 561 (1894). Löwenherz, *ibid.*, **15**, 397 (1894). Harned and Pfanstiel, THIS JOURNAL, **44**, 2193 (1922).

[2] Drushel and Hill, *Am. J. Sci.*, **30**, 72 (1910). Drushel, *ibid.*, **34**, 69 (1912).

[3] Drushel, *Am. J. Sci.*, (a) **33**, 27 (1912); (b) **37**, 514 (1914).

[4] Drushel and Dean, *ibid.*, (a) **34**, 293 (1912); (b) **35**, 486 (1913).

[5] Senter and Ward, *J. Chem. Soc.*, **101**, 2534 (1912).

[6] Reicher, *Ann.*, (a) **228**, 251 (1885); (b) **232**, 103 (1886).

[7] Dean, *Am. J. Sci.*, (a) **35**, 605 (1913); (b) **37**, 331 (1914).

[8] Slator, *J. Chem. Soc.*, **83**, 729 (1903).

of ethyl acetate[9] by hydrochloric acid is 13.8 and in the presence of 1 M potassium chloride solution is 13.9; the reaction between acetone and iodine was studied in the presence of a number of neutral salts present in concentrations from 1 to 4 N but the value of k_{35}/k_{25} was always 3.0816 ± 0.18% when a strong acid catalyst was used. The temperature coefficient of the reaction is unaffected by non-electrolytes in concentrations from 5 to 30%; indeed, one experiment[10] in 80% ethyl alcohol using sulfuric acid as catalyst gave $k_{20}/k_0 = 12.6$ as compared with 14.4 which we obtained using sulfuric acid as catalyst and water as the solvent.

It is evident, therefore, that any theory of chemical reactivity must explain the observations that catalytic reactions are usually slow and non-catalytic reactions are usually instantaneous; that the temperature coefficient is largely independent of the substrate but is always changed by a change of catalyst; and finally that the temperature coefficient is independent of influences which change widely such properties of the solvent as viscosity, dielectric constant, refractive index, thermodynamic environment, density of infra-red radiation, etc. It follows at once from those theories based on the view that only a very small fraction of the substrate molecules react (those highly energized) that each reaction would have a characteristic temperature coefficient depending on the heat of activation of the substrate, a conclusion not in accord with observations.

Protion Catalysis

On the other hand we may transfer this idea to the catalyst and we now wish to amplify the discussion given in a previous paper;[11] as before we are adopting Lapworth's view that in acid catalysis the unhydrated hydrogen ion is the catalytically active particle and that the hydrated hydrogen ion and the undissociated acid molecule possess a negligibly small catalytic activity. In order to avoid the continual use of the cumbersome term "unsolvated ion" we suggest that it be replaced by the term "protion" (Greek, *protos* = first); the unhydrated hydrogen ion is then referred to as hydrogen protion which is the same as the elementary substance proton; the unhydrated hydroxyl ion is referred to as hydroxyl protion, and other unsolvated ions in similar fashion. Hydrochloric acid is about 1000 times more active catalytically in ethyl alcohol than in water; this is explained on the assumption that the concentration of hydrogen protion in alcohol is about 1000 times the concentration in water for equal concentrations of acid. Because of this behavior and also because of the great affinity of hydrogen protion for water (about 260,000 cal. per mole) we may conclude that only an almost infinitesimally small fraction of the total hydro-

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[9] Taylor, This Journal, **37**, 551 (1915).

[10] Dawson, *J. Chem. Soc.*, **99**, 1 (1911).

[11] Rice, This Journal, **45**, 2808 (1923).

gen ion is present as hydrogen protion;[12] the same thing is assumed to be true for hydroxyl protion.

Residual Molecules

We also wish to coin another term, "residual molecule," for use in connection with chemical equilibria. If we consider the equilibrium $A + B \rightleftarrows C$, we may postulate that *A* and *B* have a very small affinity for each other so that the equilibrium concentration of *C* is very small; *C* is then referred to as a residual molecule and has the property that its concentration is proportional to the equilibrium constant of the reaction; this varies rapidly with the temperature if the heat of the reaction is large. On the other hand we may postulate that *A* and *B* have a very great affinity for each other so that now the equilibrium concentrations of *A* and *B* are very small if they are present in stoichiometric proportions; *A* and *B* are now residual molecules and their concentrations vary rapidly with the temperature depending on the heat of the reaction. In the previous paper the term "active molecule" was used but for reasons given later we wish to reserve this term for use in another connection and to apply the term residual molecule in all cases of chemical equilibrium in which the equilibrium point is largely over to one side.

Pure water may be regarded[13] as a mixture of several polymeric forms, the simple water molecules (hydrol) being present in very small concentration; this may be formulated $n\mathrm{H_2O} \rightleftarrows (\mathrm{H_2O})_n$, so that the hydrol is a residual molecule and its concentration changes rapidly with the temperature. A solution of aqueous ethyl acetate contains two residual molecules, namely hydrol and ethyl acetate hydrate; since ethyl acetate is not very soluble in water we may postulate that the $\mathrm{—COOC_2H_5}$ group has no very great affinity for water and the equilibrium $\mathrm{CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOC_2H_5.H_2O}$ is largely over to the left. The addition of hydrochloric acid to water forms a number of residual molecules as may be seen from the following equations:

$$\mathrm{HCl} + n\mathrm{H_2O} \rightleftarrows (\mathrm{H}.a\mathrm{H_2O})^+ + (\mathrm{Cl}.b\mathrm{H_2O})^- \qquad (1)$$

$$(\mathrm{H}.a\mathrm{H_2O})^+ \rightleftarrows \mathrm{H}^+ + a\mathrm{H_2O} \qquad (2)$$

$$(\mathrm{Cl}.b\mathrm{H_2O})^- \rightleftarrows \mathrm{Cl}^- + b\mathrm{H_2O} \qquad (3)$$

Since the hydrochloric acid is practically entirely dissociated and the affinity of hydrogen protion and chloride protion for water is very large, we have as residual molecules, the undissociated hydrochloric acid HCl, hydrol $\mathrm{H_2O}$, hydrogen protion $\mathrm{H^+}$ and chloride protion $\mathrm{Cl^-}$. In general, the concentrations of these will change rapidly with the temperature but the concentrations of the other molecules will change only slightly with

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[12] Lapworth [*Trans. Faraday Soc.*, **19**, 520 (1923)] discussing this problem states that he has shown "by four or five independent experimental methods that proton is hydrated to the extent of at least 99% in aqueous solution."

[13] *Trans. Faraday Soc.*, **6**, 71 (1910).

temperature. It should be noted that since Reaction 1 is exothermic (about 20,000 cal. per mole of hydrochloric acid) the concentration of the unhydrated hydrochloric acid increases exponentially with the temperature; by postulating that it is the catalyst we should have an explanation of the high temperature coefficients of reactions catalyzed by hydrochloric acid. We feel, however, that it is unreasonable to assume that when the molecule HCl is in equilibrium with water it becomes endowed with remarkable properties which it does not possess as a gas; in the absence of experimental evidence the most reasonable view is that compared with the highly reactive unsaturated hydrogen protion, all the other substances present have a negligibly small catalytic activity.

All solutions contain therefore a number of residual molecules whose concentrations change rapidly with the temperature; this change in concentration is determined by the heat of the reaction between the residual molecules and the other constituents of the solution.

The method of determining which are the residual molecules may be illustrated by the following two reactions:

$$CH_3COCH_3 + H_2O \rightleftarrows CH_3COCH_3.H_2O \qquad (4)$$

$$(CH_3)_3CCOC(CH_3)_3 + H_2O \rightleftarrows (CH_3)_3CCOC(CH_3)_3.H_2O \qquad (5)$$

Since acetone is miscible with water in all proportions we may assume that it is largely hydrated; the unhydrated acetone is therefore a residual molecule. Hexamethyl acetone is only slightly soluble in water and so we may assume that the equilibrium point of Equation 5 is largely over to the left; the hydrated hexamethyl acetone is therefore a residual molecule. From Kendall's work[14] we may conclude that the heat of formation of simple compounds of the form *AB.CD* is in general positive because "the tendency to form addition compounds is greatest at low temperatures." In an aqueous solution of acetone the concentration of unhydrated acetone will rise rapidly with the temperature; in an aqueous solution of hexamethyl acetone the concentration of the hydrate will fall rapidly with the temperature.

In general, however, the temperature coefficient of a reaction is fixed by the catalyst which usually evolves large quantities of energy on combination, as compared with the small energy changes when molecular associations take place; these can only have a comparatively slight effect on the temperature coefficient.

Active Molecules

The kinetic theory in its simple form deals with averages, and takes no account of any distribution of velocities amongst the particles. In some problems, however, the distribution of properties becomes all important and necessary for a unique solution of the problem;[15] from such considera-

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[14] See Kendall, THIS JOURNAL, **36**, 1241 (1914).

[15] See Planck, "Theory of Heat Radiation," translated by Masius, **1914**, Part III.

tions Marcelin[16] proposed an explanation for the temperature coefficients of chemical reactions. The proposition that the molecules of a reacting substance are not identical *chemically* has now been adopted by a number of workers; in all cases the postulate is made that only a minute fraction of the molecules are active chemically, these active molecules having acquired a certain critical increment of energy over the average. This somewhat revolutionary assumption is justified on the ground that it is necessary to explain, first, the existence of slow unimolecular reactions and secondly, the high temperature coefficients of chemical reactions.

With regard to the first difficulty, recent work has shown that practically all those reactions which might at first sight be considered unimolecular are really homogeneous multimolecular reactions or are catalyzed by the walls of the containing vessel: the thermal decompositions of ozone,[17] chlorine monoxide and phosgene[18] are homogeneous multimolecular gas reactions; the decomposition of nitrogen pentoxide is homogeneous but autocatalytic;[19] finally, the decomposition of phosphine which was supposed to be a unimolecular gas reaction[20] has now been shown to be a typical heterogeneous reaction[21] taking place on the walls of the containing vessel. Since we have no examples of slow unimolecular chemical reactions, the theoretical difficulties disappear.

With regard to the second difficulty, it has already been shown that if the stoichiometric equations be replaced by equations more nearly representing the reactions in solution, there are certain molecules which we now call residual molecules, whose concentrations vary rapidly with the temperature; it is postulated that at least one of the reactants in all slow reactions is a residual molecule; the rate of collision of the residual molecules with the other reactants determines the velocity of the reaction, and the change in concentration with temperature of the residual molecules determines the temperature coefficient of the reaction.

Measurement of Reaction Velocity

In the following sections we discuss reaction velocity measurements of a number of different reactions. It is desirable, therefore, to give a preliminary discussion of the reliability of such measurements, similar to that[22] given for the acetone-iodine reaction; in the usual type of chemical reaction, the rate is constantly changing so that the previous discussion of errors must be modified to meet this case.

[16] Marcelin, *Ann. phys.*, **3**, 120 (1915).

[17] Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910).

[18] Hinshelwood and Prichard, *ibid.*, **124**, 2730 (1923).

[19] Daniels, Wulf and Karrer, This Journal, **44**, 2402 (1922).

[20] Trautz and Bhandarkar, *Z. anorg. Chem.*, **106**, 95 (1919).

[21] Hinshelwood and Topley, *J. Chem. Soc.*, **125**, 393 (1924).

[22] Rice and Kilpatrick, This Journal, **45**, 1401 (1923).

Consider the simplest type of reaction, namely a bimolecular reaction in which one of the reactants is present at constant concentration; an example of such a reaction is the hydrolysis of methyl acetate by dil. aqueous hydrochloric acid. The velocity equation for this change is, $k = \frac{1}{at} ln \frac{b}{m}$, where a is the initial concentration of acid, b is the initial concentration of ester and m is the concentration of ester after t minutes. The common method of obtaining k is to titrate samples of the solution at definite time intervals throughout the course of the reaction, calculate a series of values for k and then take the arithmetic mean as representing the best value for the velocity constant. A superficial examination, however, of this formula shows that the values of k obtained are not equally reliable; in the early stages when the reaction has progressed not more than 1/10, the value of b/m is less than 1.1 and since this is contained in the logarithm it is easy to show that the error in b/m is multiplied at least 10 times in the final result, k; similarly, towards the end of the reaction m becomes very small and the error in estimating it correspondingly great.

The standard method of taking the arithmetic mean gives equal weights to all the observations, although those near the beginning and end have relatively little value; evidently the most probable value of k is given by the weighted mean instead of the arithmetic mean of the quantities.

This discussion however points to the desirability of modifying the standard procedure by making only one or two titrations near the point at which the errors in the direct measurements have least effect on the result: opening the reaction vessel at other points to withdraw samples adds but little to the precision of the final result and introduces large errors if the solutions contain volatile reactants.

The directly measured quantities from which we calculate k are t, a, b and m; the error in k caused by an error in one of the directly measured quantities is found in the usual manner by taking the partial differential of k with respect to the quantity and multiplying by its deviation.

$$\frac{\partial k}{\partial t} = \frac{1}{at^2} ln \frac{b}{m} = \frac{k}{t}; \quad \frac{\partial k}{\partial a} = \frac{1}{a^2 t} ln \frac{b}{m} = \frac{k}{a}; \quad \frac{\partial k}{\partial b} = \frac{1}{atb}; \quad \frac{\partial k}{\partial m} = \frac{1}{atm}$$

If e is the percentage error in the directly measured quantity and E is the corresponding percentage error in k, it follows that,

$$E_t = e_t; \; E_a = e_a; \; E_b = e_b \div ln \frac{b}{m}; \quad E_m = e_m \div ln \frac{b}{m}$$

The error in estimating the substance B will increase as the reaction proceeds and this error may be taken as inversely proportional to the concentration of B. We may therefore write, $e_m = e_b \frac{b}{m}$, and by substituting above we obtain: $E_m = e_b \div \frac{m}{b} ln \frac{b}{m}$. The total error E in the final result is

$E = \sqrt{e_t^2+e_a^2+e_b^2\left[\left(1/ln\,\frac{b}{m}\right)^2+\left(1/\frac{m}{b}\,ln\,\frac{b}{m}\right)^2\right]}$. The quantity $\left[\left(1/ln\,\frac{b}{m}\right)^2+\left(1/\frac{m}{b}\,ln\,\frac{b}{m}\right)^2\right]$ has a minimum value of about 3 so that if we postulate that e_t and e_a be not greater than e_b, we may, following the usual rule, neglect them in comparison with e_b which even in the best circumstances is multiplied by 3. We then obtain: $E = e_b\sqrt{1+\left(\frac{b}{m}\right)^2} \div ln\,\frac{b}{m}$. The quantity $\left(1-\frac{m}{b}\right)$ represents the fraction of the substance B that has reacted and if we plot

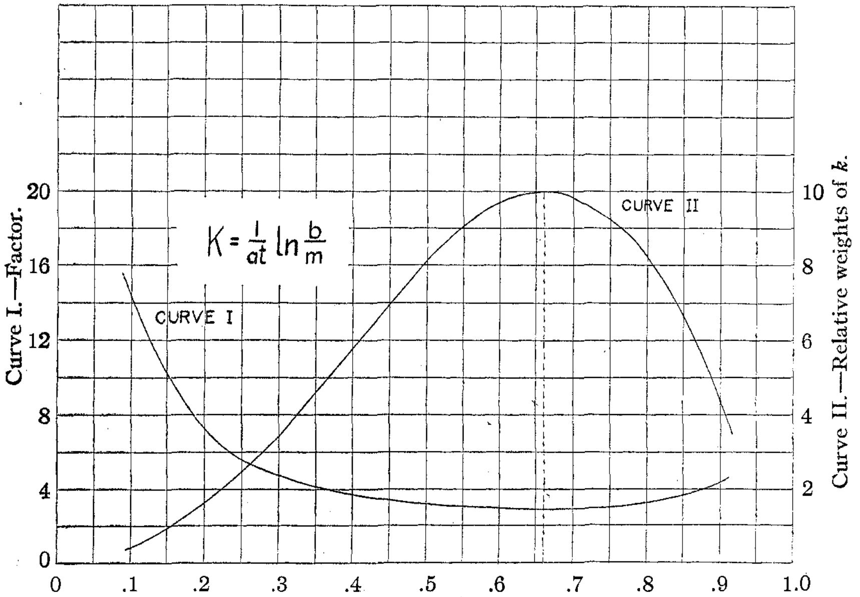

Fig. 1.—Curve I shows the relation between the fraction reacted and the factor $\sqrt{1+\left(\frac{b}{m}\right)^2} \div ln\,\frac{b}{m}$. Curve II shows the relation between the fraction reacted and the weight of the velocity constant k.

values of this against corresponding values of $\sqrt{1+\left(\frac{b}{m}\right)^2} \div ln\,\frac{b}{m}$ we can see (Fig. 1) how the errors of the direct measurement are magnified in the final result at any point during the reaction. The factor has a minimum value of 2.9 when 0.66 of B has reacted; however, from Curve II, Fig. 1, which shows the relative weights of the observations, we see that measurements between the limits of 0.5 and 0.8 of B reacted, have almost the same weight: outside of these limits the value of observations rapidly diminishes, so that very early or very late observations are practically worthless.

By following through a precisely similar argument for a reaction of the type, $2A \rightleftharpoons B + C$, for which $k = \frac{a-m}{atm}$, where a is the initial concentration of A and m is the concentration of A after t minutes we obtain, $E = e_a\sqrt{\left(\frac{m}{a-m}\right)^2 + \left(\frac{a}{a-m}\right)^2\left(\frac{a}{m}\right)^2}$. Fig. 2 shows values of the factor $\sqrt{\left(\frac{m}{a-m}\right)^2 + \left(\frac{a}{a-m}\right)^2\left(\frac{a}{m}\right)^2}$ plotted against the corresponding fraction $\left(1-\frac{m}{a}\right)$ of A reacted; the factor has a minimum value of 4.1 when 0.53 of A has reacted; however, between the limits of 0.4 and 0.6 of A reacted there is but little difference in the weight of the observations. Similar results may be obtained for a reaction of the type $A + B \rightleftharpoons C + D$, but the exact minimum point depends on the relative concentrations of A and B and must be worked out for each experiment.

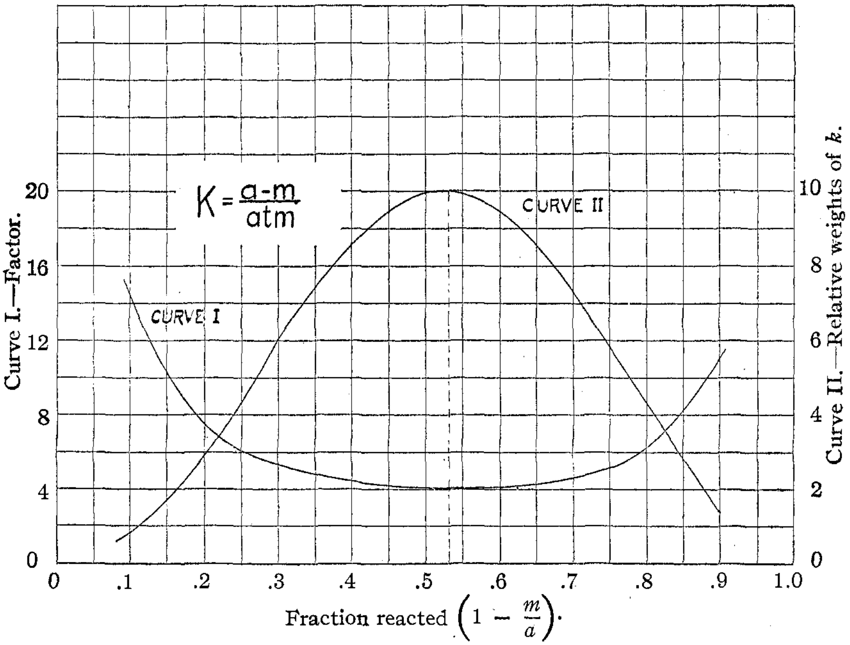

Fig. 2.—Curve I shows the relation between the fraction reacted and the factor $\sqrt{\left(\frac{m}{a-m}\right)^2 + \left(\frac{a}{a-m}\right)^2\left(\frac{a}{m}\right)^2}$. Curve II shows the relation between the fraction reacted and the weight of the velocity constant k.

Temperature Coefficients in Aqueous Solutions

The initial work in this Laboratory on the reaction acetone-iodine-hydrochloric acid in dilute aqueous solution showed that $k_{35}/k_{25} = 3.0816$,

± 0.2%, an increase which we attribute almost entirely[23] to the increase in concentration of the hydrogen protion. There are two residual molecules present which are represented in the following two equations: $H^+ + aH_2O \rightleftarrows (H.aH_2O)^+$; $2H_2O \rightleftarrows (H_2O)_2$. Provided that the hydrogen protion combines only with water and that the single water molecules (hydrol) condense mainly with themselves[24] to form polyhydrols, the temperature coefficient will always be the same. Up to moderate concentrations, the first condition is true if there is no anion of a weak acid present; up to moderate concentrations the second condition is also true because a liter of water contains approximately 50 moles.

That non-electrolytes such as ethyl acetate would not be expected to affect the temperature coefficient may be seen from the following argument. A dilute solution of hydrochloric acid in ethyl acetate is not appreciably ionized but in water is almost entirely ionized; this means that the affinity of hydrogen protion for ethyl acetate is much smaller than its affinity for water, and consequently in an aqueous solution of ethyl acetate containing some hydrochloric acid, the hydrogen protion will be combined mainly with the water. We have extended the work of Rice and Kilpatrick[22] by measuring (Table I) the effect of three non-electrolytes over a 5° range; the temperature coefficients are the same in all cases but it is interesting to note that the cane sugar causes a marked increase in the velocity.

TABLE I

EFFECT OF NON-ELECTROLYTES ON THE TEMPERATURE COEFFICIENT

	Without Non-electrolyte	0.511 *M* Cane sugar	1.84 *M* Methyl acetate	0.99 *M* Acetic acid
k_{25}/k_{20}(±0.3%)	1.8175[a]	1.8117	1.7995	1.8143
$k_{25} \times 10$ (±1.0%)	17.1	25.3	17.2	16.9

[a] In agreement with previous work.[22]

In Table II we give the results of some experiments with sulfuric acid as catalyst; the temperature coefficient is about 7% less than with hydrochloric acid, a ratio that should hold for any reaction whatsoever:[25] it should be noted also that 0.05 *M* sodium sulfate diminishes both the velocity and the temperature coefficient but both are increased by 0.43 *M* sodium sulfate;[26] if the temperature coefficients of reactions are due to residual molecules

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[23] If the concentrations of acetone, iodine and hydrogen protion were the same at the two temperatures there would be a slight difference in velocity due to the difference in kinetic energy of the particles.

[24] The water may be largely combined with another substance without affecting the temperature coefficient if the heat of hydration approximates to the heat of association of water.

[25] Lamble and Lewis, *J. Chem. Soc.*, **107,** 233 (1915), have studied the hydrolysis of cane sugar by hydrochloric acid; from their results $k_{35}/k_{25} = 4.15$. Jones and Lewis, *ibid.*, **117,** 1120 (1920), have studied the hydrolysis of cane sugar by sulfuric acid; from their results $k_{36}/k_{25} = 3.92$, a diminution of about 5%.

[26] Rice and Lemkin, THIS JOURNAL, **45,** 1896 (1923).

there is no reason to expect that increasing the velocity diminishes the temperature coefficient and we have not found any such relation.

Table II

Temperature Coefficients with Sulfuric Acid and Sulfates

	0.1 N H_2SO_4	0.15 N H_2SO_4	0.15 N H_2SO_4 0.05 M Na_2SO_4	0.097 N H_2SO_4 1.69 M $(NH_4)_3SO_4$
k_{25}/k_{20} (obs.)	1.7465	1.7462	1.7102	1.637
k_{35}/k_{25} (calc.)	2.889	2.888	2.776	2.554
$k_{25} \times 10^4$	14.3	14.4	14.0	34.0

The precision measure of k_{25}/k_{20} is $\pm 0.18\%$; the precision measure of $k_{25} \times 10^4$ is $\pm 0.6\%$.

Since we have shown that anything that affects the catalyst affects also the temperature coefficient, it remains to be shown that the other two reactants, the acetone and iodine, may be changed without affecting the value of the temperature coefficient; the acetone was replaced by its homologs and the iodine was replaced by bromine and chlorine; our experiments here were completely successful, for although the velocities varied widely in no single instance was the temperature coefficient changed in a measurable degree; an account of these experiments will be given in a succeeding communication.

A more rigorous test, however, can be made by changing over to a completely different reaction; provided that the reaction is not hydrolytic and that dil. hydrochloric acid or some other strong acid is used as catalyst, the temperature coefficient k_{35}/k_{25} should be exactly 3.0816; here, however, we met unexpected difficulties because all the examples of such reactions which we considered are accompanied by simultaneous reactions which prevent accurate measurement of the rate. We measured the rate of conversion of acetyl-chloro-aminobenzene to *p*-chloro-acetanilide[27] in dil. aqueous hydrochloric acid solution, using the improved technique developed in this Laboratory; unfortunately, we found that the main reaction is disturbed in a slight degree by a simultaneous change which prevented us from obtaining measurements of very high accuracy; however, we showed that both the velocity and the temperature coefficient are the same as in the acetone reaction to within $\pm 1\%$.

Reactions in Non-Aqueous Solutions

The velocities and temperature coefficients of several reactions have now been investigated throughout a range of solvents. Some of these reactions are ordinarily assumed to be unimolecular but on the basis of the views put forward in this paper and a previous one[11] it is necessary to postulate that they are really pseudo-unimolecular; the fact that they proceed slowly and give a unimolecular velocity constant is accounted for

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[27] Rivett, *Z. physik. Chem.*, **82**, 201 (1913). Harned and Seltz, This Journal, **44**, 1475 (1922).

by assuming the presence of a minute trace of a catalytic impurity in the solvent; such a residual molecule present in constant concentration accounts for the existence of a slow reaction and a unimolecular constant. While all the supposed unimolecular gas reactions have now been shown to be bimolecular or catalyzed by the walls of the vessel, this has been done for only a few reactions in solution. A solution of *n*.-nitrocamphor gradually changes to the pseudo form and the velocity of change can be conveniently followed by the polarimeter; Lowry and Magson[28] studied the rate in a number of different solvents purified with the greatest care. A chance observation, however, led them to the conclusion that all their measurements of the velocity were not characteristic of the particular solvent at all, but were simply due to minute traces of alkaline impurities, which are still present even after the most rigorous purification: by adding a trace of carbonyl chloride to destroy aminic impurities, and by preserving the solutions in silica flasks, they showed that the isomeric change is a catalytic phenomenon which does not occur in the absence of hydroxyl ion.[29] Similar results have been obtained by Meyer and his co-workers[30] for aceto-acetic ester; they showed that the two forms are stable except when in contact with glass or in the presence of some other source of hydroxyl ions.

Bimolecular reactions such as that between alkyl halides and organic bases have also been studied in a number of different solvents. The equation representing the reaction between ethyl iodide and tri-ethyl amine is, $C_2H_5I + (C_2H_5)_3N = (C_2H_5)_4NI$; now if this equation were true the reaction would be instantaneous, and consequently we must postulate the existence of a residual molecule as one of the reactants, in this case possibly hydroxyl protion, since one of the reactants is basic. The rate of the reaction would then be determined by the rate of collision of the hydroxyl protion with the other reactants, and furthermore the temperature coefficient of the reaction is fixed by the change in concentration with temperature of the hydroxyl protion. Now it has already been shown for aqueous solutions that the addition of substances which change the character of the solution, only slightly affects the temperature coefficient; consequently, we are led to infer that a given reaction will have approximately the same temperature coefficient in a range of solvents if the catalyst or other residual molecule is the same throughout. This conclusion will now be tested by considering published work.

In measuring the rates of these reactions the procedure in all cases is

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[28] Lowry and Magson, *J. Chem. Soc.*, **93**, 107, 119 (1908).

[29] The difficulty of obtaining and preserving solvents free from catalyst may be gaged from one experiment in which they show that an amount of piperidine in benzene equivalent to 0.1 g. per ton of benzene increases the velocity considerably.

[30] Meyer and Schoeller, *Ber.*, **53**, 1410 (1920). Meyer and Hopff, *ibid.*, **54**, 579 (1921).

to estimate one of the reactants by titrating measured portions of the solution with a suitable standard reagent; usually the initial titer is about 10 cc. and the final titer about 7 cc., with two or three intermediate titrations; owing to the difficulties of this work we may assume that the analytical error is at least ±1%; from Fig. 2 we see that the error in the velocity will then be ±4% if a measurement is made when the reaction is half over; unfortunately, in practically all cases the measurements were confined to the early stages of the reaction, so that the error in determining the velocity may be conservatively placed at ±5%; further, since two velocity measurements are necessary to determine a temperature coefficient, the error is $\sqrt{5^2 + 5^2} = 7\%$.

Several studies have been made of the reaction between organic bases and alkyl halides; Preston and Jones[31] who studied the reaction of allyl bromide with dimethyl aniline and tri*iso*amylamine obtained a mean value for $k_{35}/k_{25} = 2.28$. Hawkins[32] studied the reaction between allyl bromide and pyridine in seven solvents and obtained the mean value of $k_{38\cdot3}/k_{28\cdot3} = 2.06$, average deviation ±5.6% and the maximum deviation ±9%; from the value $k_{38\cdot3}/k_{28\cdot3} = 2.06$ we obtain $Q = 13.500$, and hence $k_{35}/k_{25} = 2.10$. The reaction between ω-bromo-acetophenone and aniline[33] has been studied in eight different solvents; if we exclude one of the solvents, benzene, the mean value of $k_{37\cdot8}/k_{27\cdot8} = 2.04$, average deviation ±5.0%, maximum deviation ± 7.4%; for benzene $k_{37\cdot8}/k_{27\cdot8} = 1.53$ which is 25% lower than the mean value.

The decomposition of oxalic acid[34] in sulfuric acid solution is ordinarily considered to be a unimolecular reaction;[35] it is probable, however, that we are dealing here with an example of hydrogen protion catalysis and that the rate of the reaction is determined by the rate of collision of hydrogen protion with a sulfuric acid-oxalic acid complex; this explanation is supported by observations that small quantities of water greatly retard the reaction and by the approximate identity of the temperature coefficient for solutions containing various quantities of water; thus from Lichty's results we obtain the following calculated values for k_{35}/k_{25}.

% H_2O present	0.1	0.6	3
k_{35}/k_{25} (calc.)	4.42	4.80	4.94
Temperature range, °C.	25–45	45–70	70–98

The analytical difficulties here are great and these differences are probably within experimental error.

The reaction between sodium β-naphthoxide and ethyl iodide was stud-

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[31] Preston and Jones, *J. Chem. Soc.*, **101**, 1930 (1912).

[32] Hawkins, *ibid.*, **121**, 1170 (1922).

[33] Cox, *ibid.*, **119**, 142 (1921).

[34] Lichty, *J. Phys. Chem.*, **11**, 225 (1907).

[35] See Taylor, *ibid.*, **27**, 322 (1923). Christiansen, *ibid.*, **28**, 145 (1924).

ied[33] in nine alcohols; the mean value of $k_{47\cdot 8}/k_{37\cdot 8} = 2.80$, average deviation 2.9%, maximum deviation 4.7%.

It is doubtful, therefore, whether the observed variations within each of these classes of reactions are greater than the experimental errors; we must conclude from the experimental evidence available that a variation of solvent has but little effect on the temperature coefficient.

Summary

1. The temperature coefficient of a reaction depends on the nature of the catalyst and is comparatively independent of the nature of the substrate.
2. Double compound formation of the substrate with one of the constituents of the solution may affect the temperature coefficient; since a small heat change is usually associated with double compound formation, this effect can only be small compared to the effect of a catalyst, whose combinations are usually associated with large energy changes.
3. We suggest that unsolvated ions be called "protions;" acid catalysis is attributed to the "hydrogen protion" and catalysis by alkalies to the "hydroxyl protion."
4. The temperature coefficient of a reaction is fixed by certain molecules which we call "residual molecules;" these are present in very small concentration and are connected with an equilibrium constant in such a way that their concentrations vary rapidly with temperature.
5. For a reaction to proceed with measurable speed, at least one of the reactants must be a residual molecule; on this basis the existence of slow unimolecular reactions is denied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY COEFFICIENTS OF DILUTE AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE, THALLOUS CHLORIDE AND LEAD NITRATE

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Three quite independent experimental methods have been used for the accurate determination of the activity coefficients of dilute aqueous salt solutions. As examples of the precise application of these three methods we may mention hydrochloric acid by the electromotive force method, thallous chloride by the solubility method and potassium chloride by the freezing-point method.[1]

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[1] For a detailed discussion of these methods and a summary of the results see (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, 1923, Chapters XXVI, XXVII and XXVIII,