The nature of the burn was further confirmed by the fact that it took long to heal, traces of it were visible Mar. 31, 1908, or four months later.

To further test the theory, at Dr. Abbe's suggestion, the experiment was repeated on Dec. 21, and to eliminate the personal equation a sheet of lead, perforated with five holes, was interposed between the Cramer X-ray "X" plate, enclosed in the usual black and yellow papers, and the portion of the furnace corresponding to the height of my knee from the floor, while the zinc was distilled. There is a crack around the furnace at this point, and it was about there that the fumes of burning zinc could be seen within the furnace. Alloy and lampblack were again used in the charge. The plate was exposed for 1 hr. and 17 min. at a distance of 2 ft. from the furnace, and a thermometer placed beside the plate showed a temperature ranging from 25° to 35°, with one time a temperature of 42°.

The plate was given to a photographer to be developed along usual lines, but he was not told what might appear on the plate. The developed plate and a positive printed from it show the five holes in the lead covering plate and thus confirm the diagnosis of the nature of the burn.

Later, other plates were exposed during runs but no distinct effects produced. Nor was there any similar result to the first obtained when Messrs. Stone and Riggs kindly exposed similar plates behind the perforated lead plate to the light of burning zinc at the furnaces of the New Jersey Zinc Company.

Both the burn and the effect on the X-ray plate were produced when alloy and lampblack were used. When coke, charcoal, and gas carbon were used with the alloy no photographic evidence was obtained. The lampblack was purchased in open market, as also the zinc, calcium chloride, and sodium, the other chemicals used. The fuel was either ordinary charcoal or in the later experiments coke or coal or both together. The Dixon crucibles and covers were new.

As an opportunity has not presented itself for me to repeat these experiments methodically and determine the cause of the phenomena the facts are placed on record in the hope that sometime an explanation will be forthcoming.

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NEW YORK, N. Y.
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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE INFLUENCE OF TEMPERATURE IN ACID CATALYSIS.

BY HUGH STOTT TAYLOR.

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Since the suggestion was put forward by Goldschmidt,[1] Snethlage[2]

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[1] *Z. physik. Chem.*, **70**, 627 (1910); **81**, 30 (1912).

[2] *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 211 (1913).

and Acree[1] that, in addition to the hydrogen ion, the undissociated molecule of an acid has a catalytic effect, interest in reactions catalyzed by acids has been markedly stimulated. Snethlage amplified the observation by calling attention to the fact that the stronger the acid, or the greater its dissociation constant, the more active was the undissociated molecule catalytically as compared with the hydrogen ion.

In a series of researches the author, acting upon the above suggestion, showed that the theory was quantitatively applicable, in addition to the catalytic reactions of acids in organic solvents as studied by the investigators cited above, to reactions in aqueous solutions. The first investigation[2] showed that neutral salt action in ester catalysis was independent of the ester substrat, that, therefore, the existence of an equilbrium of active and inactive molecules of the ester substrat, such as had earlier been suggested by Arrhenius to account for the high temperature coefficient of such reactions, was rendered improbable and that an explanation of neutral salt action would probably be such as involves only the catalyzing liquid and not the ester present.

It was next shown[3] that the experimental results of simple acid catalysis and of the accelerating influence of neutral salts in aqueous solutions could be interpreted more closely than was hitherto possible, and with an accuracy as considerable as the present fairly large experimental error will permit, if the activity of the undissociated molecule be assumed. Also, the relation of Snethlage between activity and strength of acid was shown to be applicable in aqueous solutions.

These conclusions received independent confirmation in a research of Dawson and Powis[4] on the catalytic influence of acids on the keto-enol transformation of acetone in aqueous solutions. With the aid of the then available literature the author was led[5] to the formulation of a quantitative relation between catalytic ratio of undissociated molecule and hydrogen ion activities and the affinity constants of various acids. It was suggested that a simple mathematical relationship, *viz.*, that the affinity constant was equal to the square of the catalytic ratio, existed between the two; that the strength of the acid is the primary factor in the determination of the catalytic ratio and that deviations from the values calculated according to the equations deduced in the paper should be sought for in the variations of the nature of the reaction studied.

Somewhat later,[6] MacBain and Coleman, in a recalculation of some old data of Arrhenius on the dissociation of weak acids, called attention to the

[1] *Am. Chem. J.*, **48**, 352 (1912).

[2] *Medd. fr. K. Vetenskaps. Nobelinst. Bd.* **2**, Nr. 34 (1913).

[3] *Loc. cit.*, Nr. 37 (1913).

[4] *J. Chem. Soc.*, **104**, 2135 (1913).

[5] *Z. Elektrochem.*, **20**, 201 (1914).

[6] *J. Chem. Soc.*, **105**, 1520 (1914).

fact that some measurements of Arrhenius on the inversion of cane sugar by hydrochloric acid, in presence and absence of potassium chloride at varying temperatures, could be used for the determination of the ratio $K_m : K_h$.[1] These data, while revealing internal evidence of a certain amount of experimental error, made it appear probable, according to the authors, that the ratio K_m/K_h decreases with rise of temperature. The actual figures are given in Table I.

TABLE I.

Potassium chloride.	0.05*N* HCl at 25°.	0.01*N* HCl at 38°.	0.0005*N* HCl at 52°.
0.025	2.99	1.45	1.13
0.125	2.77	1.70	1.30

It was further suggested that this effect had not hitherto been suspected and might serve to explain some of the deviations from the quantitative relationship proposed somewhat earlier by the author. Actually, however, the point in question had been noted and the same calculations had been made with essentially the same result, but it was felt that, in view of the extraordinary sensitivity of the ratio to small experimental errors as evidenced by the author's own results under more favorable conditions, it would be better to defer discussion of the point until some more definite evidence was accumulated. Certain experiments were, however, carried out in the laboratory of Arrhenius by the author having a bearing on the point in question, which will be presented below, together with other experimental data just available from the literature. MacBain and Coleman nevertheless point out later in their paper that, if a constant value for K_m/K_h of 1.5 is applied throughout their calculations for all temperatures, all the results with the exception of the first three are within 4% of the predicted rates; and that of the three discordant experiments one diverges as much in one direction as another does in the opposite. It is obvious, therefore, that a decision as to whether the catalytic ratio is a variable with temperature remained, as a result of MacBain and Coleman's investigations, an open question.

There has recently appeared[2] a paper on catalysis which supplies data utilizable for a calculation of the temperature influence in ester catalysis as regards the catalytic ratio. The hydrolysis of methyl acetate at vary-

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[1] The reaction constant is regarded as due to the sum of two catalytic activities, that of the hydrogen ion K_h and that of the undissociated acid K_m. These activities are regarded as operating in degrees proportional to their concentrations as calculated from the conductivity data. An equation is obtained of the form

$$n_h K_h + n_m K_m = R$$

where n_h or n_m are the respective concentrations of ion or molecule, R the reaction constant. From two such equations K_m and K_h may be evaluated and the catalytic ratio, $K_m : K_h$ obtained.

[2] Lamble and Lewis, *J. Chem. Soc.*, **105**, 2330 (1914).

ing concentrations of hydrochloric acid has been studied at 25° and 35° and the degrees of dissociation and hydrogen ion concentrations of the acids employed have been obtained. The range of concentrations chosen was large and the data obtained seemed to offer a good opportunity for making the calculations required. The general conclusion is drawn that there is no tendency at all for the temperature-coefficient of a strongly catalyzed reaction to be less than that of a weakly catalyzed reaction, a deduction contrary to what one would have expected on the conception of active and inactive molecules of ester substrat, in agreement, therefore, with the earlier conclusions of the author from work on neutral salt action with varying ester.

The experimental results of Lamble and Lewis have been calculated to give the values of K_m and K_h and the ratio K_m/K_h at the two temperatures employed. The method of calculation has been described in detail in various earlier communications so that it calls for no further detailment here. The six possible combinations of pairs of data as to molecular and ionic concentrations and to catalytic activity at each temperature have been calculated and the results are set forth in Table II.

TABLE II.

	25°.			35°.					
No. of expt.	Acid normality.	H˙ ion conc.	Reaction const.	Acid normality.	H˙ ion conc.	Reaction const.	From expts.	25° K_mK_h.	35° K_mK_h.
1	0.5024	0.4503	3.510	0.5024	0.4400	8.836	1 & 2	1.94	4.62
2	0.8275	0.7047	6.001	0.8275	0.7086	15.26	1 & 3	4.60	1.88
3	1.800	1.422	16.09	1.935	1.422	37.84	1 & 4	2.36	1.91
4	2.429	1.718	20.78	2.92	1.718	63.47	2 & 3	9.62	1.54
							2 & 4	0.945	1.77
							3 & 4	—0.71	1.95

If the theory of Goldschmidt, Snethlage and Acree be correct, it is obvious that the ratio K_m/K_h as calculated from a series of acid dilutions should be constant. Observation will show that at 35° with one exception, in which experimental errors would certainly be greatest in their effect on the calculation, the requirement is fulfilled. At 25° it will readily be seen that the values obtained are by no means constant. Closer examination reveals, however, that only those calculations in which Expt. 3 was utilized were the deviations considerable, yielding in the one case a negative result. The experimental results were therefore examined more closely and led to the conclusion that in all probability some fairly considerable error had crept into the determination. For example, it is well known—and the data of Lamble and Lewis confirm this—that the reaction constant in catalysis of esters by hydrochloric acid increases at a slightly more rapid rate than does the normality of the acid; in other words, the graph of the two sets of values yields a curve concave towards the axis of normality. Lamble and Lewis' results were plotted therefore in this manner and the plot for Expt. 3 was found to lie some considerable distance from the curve through the remaining points and concave to the axis of normality. Fortunately a determination made by the authors at a concentration 0.1024 *N* could be included to facilitate this conclusion. Further, an examination of the values used for the degree of dissociation at the concentration employed in Expt. 3, *viz.*, 1.80 *N*, showed the rather surprising result that the degree of dissociation at 1.80 *N* was equal to that at 1.28 *N* and amounted to 0.7900, while at a concentration 0.6 *N* higher the dissociation had fallen rapidly again to 0.7071. It is not surprising, therefore, that with two such factors operating in the calculations the results obtained should show some irregularity. Of the remaining three it cannot be said, however, that they show values higher than those obtained in the calculations at 35°. The mean of the three calculations at 25° is 1.75 while of the five concordant values at 35° the mean is 1.81.

Happily, however, a surer test than the above may be applied to the question of the variability or non-variability of the ratio K_m/K_h with temperature. Dawson and Powis obtained in their investigations a most excellent series of values for K_m and K_h at 25° with hydrochloric acid, yielding as a mean value from a series of seven observations 1.77 for the catalytic ratio. This value is in remarkably good agreement with the value calculated from the data of Lamble and Lewis at the two temperatures.

It would seem, therefore, that the suggestion of MacBain and Coleman as to the decrease of the activity ratio with temperature is untenable in the light of the above results. Confirmation of this view seems forthcoming in the data presented below, compiled from experimental work of the author. In some earlier work on neutral salt action in ester catalysis it had been noted that, according to Price[1] and Senter[2] the action is not markedly influenced by temperature. That conclusion was tested experimentally by the author over a wider range of temperature than had previously been employed. The velocity of hydrolysis of ethyl acetate using 0.1 *N* hydrochloric acid, alone and in presence of normal potassium chloride, was studied at the three temperatures 0°, 25°, and 40°. The experimental values communicated below represent the means of at least two concordant experiments. The value D expresses the percentage increase in the reaction constant due to the presence of the salt, assuming that the change in the reaction constant is proportional to the change of hydrogen ion concentration.[3]

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[1] *Ofvers. af Vet. Akad. Forh.*, **9**, 934 (1899).

[2] *Z. physik. Chem.*, **70**, 516 (1910).

[3] Kay, *Proc. Roy. Soc. Edin.*, **22**, 484 (1897); Taylor, *loc. cit.*, No. 34.

TABLE VI.

Temp.	Normality of acid.	Normality of neutral salt.	Velocity constant. K.	Hydrogen ion concentration. α.	$D = 100\frac{K_2 - K_1\,\alpha_2/\alpha_1}{K^1\,\alpha_2/\alpha_1}$.
0°	0.10	...	2.056	0.916	....
	0.10	1.0	2.480	0.777	42.2
25	0.10	...	28.29	0.916	....
	0.10	1.0	34.45	0.777	43.6
40	0.10	...	109.4	0.916	....
	0.10	1.0	132.9	0.777	43.2

Assuming, therefore, as has frequently been shown, that at these concentrations the degree of dissociation of the acid varies but slightly with temperature, it is obvious that the values for K_m/K_h obtained at the various temperatures will also be concordant. In other words, as pointed out previously by the author, the ratio of the catalytic activities of undissociated molecule and hydrogen ion is primarily a function of the strength of the acid and therefore of its dissociation constant when such can be derived; that therefore, since the dissociation constant varies but little with temperature, the catalytic ratio will itself be relatively independent of temperature and not, as originally suggested by MacBain and Coleman, possess a large temperature coefficient.

Attention might here be directed also to the method employed by Lamble and Lewis for the determination of the temperature coefficient of these reactions. As pointed out by them, so long as the same hydrogen ion concentration persists at the two temperatures in the corresponding experiment, the concentration of the catalyst remains the same, whether the catalyst be the hydrogen ions, the undissociated molecules or both. But at the higher concentrations employed by them the condition is no longer fulfilled, for a hydrogen ion concentration of 1.422 corresponds to a 1.800 *N* acid at 25° and to a 1.935 *N* acid at 35°. It is evident, therefore, that if the undissociated molecule be considered active, then of the two solutions, at the same hydrogen ion concentration, the acid of normality 1.935 at 35° will be the more active, since its concentration will be 0.513 in respect to undissociated molecule, as compared with 0.378 in the case of the acid of normality 1.800 at 25°. Since the undissociated molecule appears from the previous calculations to be 1.8 times as active as the hydrogen ion, it is evident that the temperature coefficient K_{35}/K_{25}, as deduced by them, is in reality a little too large as the total concentration of catalyst is greater at the higher temperature. If this factor is taken into consideration, and the reaction constant at 25° be re-checked, it is very probable that the temperature coefficient K_{35}/K_{25} at the two higher concentrations would more closely correspond with the very concordant value found by them in the more dilute solutions, where no divergence exists between acid normality and hydrogen ion concentration at the two temperatures.

Summary.

An examination of recently available literature on catalysis of esters at varying temperatures, together with some new experimental data on neutral salt action in ester catalysis at 0°, 25°, and 40° is shown to yield the conclusion that the ratio of the catalytic activities of undissociated molecule and hydrogen ion does not possess a considerable temperature coefficient such as was suggested by MacBain and Coleman, but, on the contrary, is independent of temperature. The importance of a consideration of the activity of the undissociated molecule in calculations of reaction constants in acid catalyses has been emphasized.

PRINCETON, N. J.

ORGANIC OXONIUM COMPOUNDS.

I. DIMETHYLPYRONEHYDROCHLORIDE.

BY H. N. K. RÖRDAM.

Received January 6, 1915.

Theoretical Part.

Since the discovery by Collie and Tickle[1] of the addition compounds of dimethylpyrone with acids, numerous investigations have been made upon this matter. That these and similar addition products of organic compounds containing oxygen are real and stable compounds and chemical individuals has been shown in researches by several authors, among many others recently by Kendall,[2] and Maas and McIntosh.[3] As to their being oxonium compounds, the question is still open. Not one single experimental fact is known, which absolutely compels us to see in them anything more than molecular compounds in which the acid is bound in the manner that the water of crystallization is in crystallized salts. If the addition compounds with acids are true oxonium compounds, they must be salts; but although many observations have been made which may suggest a salt character, only evidence, not certainty, has been won. The conductivities of these compounds as well as the depression of the freezing point of their solutions have been measured by several investigators. It was found that their solutions were conductive, and that the freezing point was more depressed than the number of dissolved mols would account for. From these measurements constants of dissociation for dimethylpyrone as a base were calculated. It is, however, evident that the results would be the same if only dissociation into components, for instance for dimethylpyronehydrochloride after the scheme:

$$C_7H_8O_2.HCl \rightleftarrows C_7H_8O_2 + HCl$$

takes place in the solutions. To prove that dimethylpyronehydrochloride is a real salt it must first be proved that, besides the above-named

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[1] *J. Chem. Soc. Trans.*, 1899, 710.

[2] THIS JOURNAL, 36, 1222.

[3] *Ibid.*, 34, 1273 and 35, 535.