capacity since it is soluble in pyridine and also inert toward Karl Fischer reagent. The type of catalysis involved is not known, but the high electrical conductivity of sodium iodide in pyridine solution observed in this Laboratory may have some bearing upon its catalytic activity. In Fig. 1 the effect of increasing concentrations of sodium iodide on hydrolysis is shown; curves for five representative anhydrides are presented. It is interesting to note that hydrolysis of phthalic anhydride was 99% complete even without sodium iodide.

Compounds Investigated.—All anhydrides were used without further purification. Glutaric anhydride was prepared from the acid by the method of Mol.[5] Phthalic anhydride (Aero Brand) was obtained in flake form from American Cyanamid Corporation. All others were Eastman Kodak Co. chemicals. As in the previous investigations, a simple "dry manipulator" was used to dispense the solid anhydrides.[2]

Reagents.—Ten per cent. sodium iodide in pyridine containing about 1% of water was prepared by making 100 g. of Baker C. P. analyzed sodium iodide and 8 ml. of water up to 1 liter with Baker C. P. pyridine.

Analytical Procedure.—A sample containing 8–10 millimoles of anhydride is weighed into a 250-ml. glass-stoppered volumetric flask. Using a precision pipet, 25 ml. of the pyridine reagent is added. The flask, together with a blank containing 25 ml. of the reagent, is placed in a water-bath at 60±1°. The stoppers are loosened momentarily to allow for expansion of included air, tightened, and the flasks heated for one hour. After being allowed to cool spontaneously to room temperature, the excess water is titrated with Karl Fischer reagent. The total anhydride is measured by the difference in titer between water added (blank titer) and water found by titration after reaction.

Interfering Substances.—Easily hydrolyzed esters, as stated above, do not interfere. This was established in experiments with methyl formate, methyl acetate and ethyl acetate.[6] Since at low temperatures (0° or below) the reaction of anhydrides with water is generally very slow, the water content can be obtained by direct titration of the chilled sample with Fischer reagent. When this water is taken into consideration, analyses by the above method will give the correct anhydride content of such mixtures.

Summary

1. An alternative procedure for the quantitative determination of carboxylic acid anhydrides has been described. The method depends on complete hydrolysis of the anhydride by a small excess of water in the presence of pyridine, with sodium iodide as a catalyst, and subsequent titration of the residual water with Karl Fischer reagent.

2. Analytical data for eleven anhydrides are tabulated.

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[5] Mol, *Rec. trav. chim.*, **26**, 373 (1907).

[6] The determination of anhydride in the presence of carbonyl compounds is being investigated.

WILMINGTON, DELAWARE RECEIVED APRIL 9, 1941

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY AND THE UNIVERSITY OF ROCHESTER]

Thermal Reactions Promoted by Diacetyl[1]

BY F. O. RICE AND W. D. WALTERS[2]

In a number of investigations it has been shown that free radicals produced either thermally,[3] or photochemically,[4] can markedly accelerate the decomposition of other compounds and frequently can induce decomposition at temperatures at which the pure compound alone is stable. However, the introduction of methyl groups into acetone at 400° or below does not initiate a chain decomposition of acetone.[4,5] On the other hand, in the present study of the effect of diacetyl on the decomposition of acetone at 526°, it was discovered that a small amount of diacetyl accelerates the decomposition. Presumably this indicates that diacetyl acts as a source of free radicals in the neighborhood of 500° just as azomethane[3b] and ethylene oxide[3c] do at lower temperatures. Therefore, an investigation of the influence of small quantities of diacetyl on the rate of decomposition of various organic compounds, as well as on the polymerization of ethylene, was undertaken.

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[1] In part from a dissertation submitted by W. D. Walters to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Wm. R. Warner Fellow of the Johns Hopkins University, 1934–1938. Present address, University of Rochester, Rochester, N. Y.

[3] (a) Frey, *Ind. Eng. Chem.*, **26**, 200 (1934); (b) Allen and Sickman, THIS JOURNAL, **56**, 2031 (1934); (c) Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936); (d) Echols and Pease, *ibid.*, **58**, 1317 (1936).

[4] Leermakers, *ibid.*, **56**, 1899 (1934).

[5] Rice, Rodowskas and Lewis, *ibid.*, **56**, 2497 (1934).

Experimental

C. P. acetone was further purified by several fractionations, the middle two-thirds being saved from each distillation. Absolute alcohol, which had been dried over magnesium amalgam, was fractionated in a similar manner. The boiling points of the acetone and ethyl alcohol under 760 mm. were 56.3 and 78.2°, respectively. The diacetyl was treated similarly to that used in a previous investigation.[6] C. P. diethyl ether and Eastman Kodak Co. acetaldehyde were used without further purification. The purity of the ethylene, obtained from the Ohio Chemical Company, was 99.5%.

The reaction vessel and furnace were essentially the same as the apparatus previously employed.[6] In the experiments in which mixtures of diacetyl with either acetone, diethyl ether, or acetaldehyde were prepared, the samples were mixed and the charges were introduced into the reaction vessel by a device similar to that described by Rice and Polly.[7] In the runs in which mixtures of diacetyl with either ethyl alcohol or ethylene were used, samples were prepared by expanding a known amount of diacetyl into a large mixing bulb and then adding the other component. By proper manipulation of the stopcocks a sample from this bulb was allowed to flow into the reaction vessel. The rate of reaction was then determined by pressure measurements using a mercury manometer.

To analyze for ketene resulting from the decomposition of acetone, two methods were used to bring about reaction of ketene with water. In the first method, the product gases from the reaction vessel were expanded into a one liter bulb containing water. After allowing ten hours or more for absorption, the acetic acid formed was titrated with dilute alkali. In the second method, the product gases were led through a long trap cooled in liquid air. The ketene, as well as the undecomposed acetone, condensed out and the permanent gases were removed. After removing the liquid air, water was allowed to run into the trap with the system still closed. After the same absorption period as above, the acetic acid was titrated.

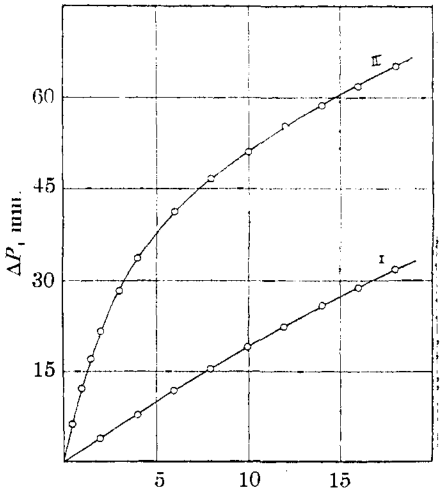

Fig. 1.—Thermal decomposition of acetone at 526°: Curve I, pure acetone at 197 mm.; Curve II, acetone at 197 mm. containing 0.94% diacetyl.

Results

Decomposition of Acetone.—The data from measurements of the rate of decomposition of acetone in the presence of diacetyl are shown in Table I. From the initial rates of pressure increase $(dP/dt)_0$ at 526°, it is evident that diacetyl accelerates the decomposition of acetone very markedly near the beginning of the decomposition. However, as the diacetyl decomposes, the effect dies away before all the acetone has decomposed; so that after twenty minutes the rate has almost returned to the value it would normally have at that percentage decomposition. That this accelerated initial rate is not merely the result of the combined independent decompositions of diacetyl and acetone can be seen from Fig. 1, or from a comparison of the pressure increases which have occurred after seventeen minutes, ΔP_{17-0}, for acetone alone and for acetone containing diacetyl, given in Table I. Most of the experimental error in these runs can be attributed to the difficulty of handling small amounts of diacetyl and to the variations in temperature. The additional amount of decomposition in the presence of diacetyl corresponds to twelve molecules of acetone decomposed per molecule of diacetyl added at the higher diacetyl concentration

TABLE I

PROMOTED DECOMPOSITION OF ACETONE AT 526°

P_0, mm.	Diacetyl, %	$(dP/dt)_0$, mm./min.	ΔP_{17-0}, mm.
198	0.00	1.9	29.6[a]
197	.11	3.7	37.3[b]
198	.16	5.1	41.5
197	.22	5.9	45.5[b]
198	.30	7.2	49.2
200	.40	7.0	49.6
200	.56	8.3	54.1
199	.73	9.2	56.8[b]
197	.93	11.9	63.8[b]
204	1.12	13.5	67.9
197	1.35	13.3	67.7
150	0.00	1.4	22.2[b]
150	.30	5.0	38.0
149	.80	7.0	44.1
152	1.50	10.3	53.8
101	0.00	0.96	15.6[b]
101	.19	2.7	23.5
101	.42	3.9	26.4
100	1.19	5.5	32.6
101	2.32	9.4	45.4

[a] Average of seven runs. [b] Average of two runs.

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[6] Rice and Walters, *J. Chem. Phys.*, **7**, 1015 (1939).

[7] Rice and Polly, *ibid.*, **6**, 273 (1938).

and to approximately forty molecules at the lower concentration.

At 506° where a slight induction period[8] was observed with pure acetone, addition of 0.3% diacetyl resulted in the elimination of the induction period and acceleration of the rate above that of the maximum rate with pure acetone. Likewise at 540° an acceleration of the rate of decomposition of acetone by diacetyl was observed.

Since ketene is one of the products of the normal decomposition of acetone,[9] analyses for ketene were carried out to determine whether the promoted and ordinary decompositions were similar. If so, the accelerated rate of decomposition in the presence of diacetyl should result in an increased rate of formation of ketene. The results of the analyses of the products removed from the reaction vessel after two and one-half minutes are shown in Table II. Satisfactory agreement was obtained for the two methods of transforming ketene into acetic acid: A, denoting expansion of the products into the large vessel containing water, and L, denoting condensation of ketene at liquid air temperatures, followed by addition of water to the closed trap. The fact that the amount of ketene formed in the products from the promoted decomposition is considerably greater than that formed in the same time in the normal decomposition indicates that the promoted decomposition leads to the same products as the normal decomposition. As would be expected, with larger amounts of decomposition, the per cent. yield of ketene is less. In the promoted decomposition a small amount of ketene will be produced from the decomposition of diacetyl.[10,6] Although it is difficult to estimate the exact amount of ketene resulting from the decomposition of diacetyl, it should not exceed 5% of the analyzed quantity.

TABLE II

KETENE FORMED IN THE DECOMPOSITION OF ACETONE AT 527°. REACTION TIME, 2.5 MIN.

P_0, mm.	Diacetyl, %	ΔP, mm.	Method	Ketene press., mm
176	0.0	5.3	A	5.2
164	0.0	4.7	L	4.9
167	1.19	23.5	A	14.0
166	1.19	23.9	L	13.6

In a series of experiments at 526° using acetone containing small percentages of other substances, such as oxygen, azomethane, azoisopropane, ethylene oxide, trimethylamine, diethyl ether, dimethyl ether, acetonyl acetone, or acetyl acetone, it was found that none of these substances accelerated the decomposition as much as diacetyl. Addition of oxygen, 1% of which caused approximately a 50% increase in the initial rate, or addition of ethylene oxide did cause a noticeable acceleration, but the other substances had very little, if any, effect.

From observations on the stability of the acetyl radical,[11] the possibility of the formation of diacetyl as an intermediate in the normal decomposition of acetone did not appear very likely. Moreover, in two earlier investigations,[12,11b] it had been reported that no diacetyl was detected in the products from the thermal decomposition of acetone. However, the experimental conditions were considerably different from those employed in the usual kinetic studies. Therefore, since diacetyl was more effective than any of the other compounds in promoting the decomposition of acetone, we decided to test for the presence of diacetyl during the decomposition of acetone. This was of particular interest since the time necessary for the building up of a small concentration of diacetyl might be the cause of the induction period.

Experiments at 200 mm. pressure were carried out in a twelve-liter reaction vessel at temperatures of 464, 468 and 491°. The amounts of decomposition in the three experiments were 1.34, 2.40 and 11.0%, respectively. The products which had been collected in a trap cooled with liquid air were divided into two samples for analysis. A modification of the method described by Barnicoat,[13] which depends on the formation of nickel dimethylglyoxime, was used to test for diacetyl. The amounts of hydroxylamine hydrochloride and sodium acetate were increased over the quantities suggested by Barnicoat because of the presence of acetone. In none of the experiments was any diacetyl detected. Several experiments were also made to determine how small an amount of diacetyl could be detected in the presence of acetone and the products from the acetone decomposition. Samples containing 0.025

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[8] In the decomposition of acetone an induction period which becomes more pronounced at lower temperatures was first observed by Allen, THIS JOURNAL, **58**, 1052 (1936).

[9] Hurd and Tallyn, *ibid.*, **47**, 1427 (1925); Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

[10] Hurd and Tallyn, THIS JOURNAL, **47**, 1779 (1925).

[11] (a) Spence and Wild, *Nature*, **138**, 206 (1396); *J. Chem. Soc.*, 352 (1937); (b) Glazebrook and Pearson, *ibid.*, 567 (1937); (c) Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[12] Rice, *Trans. Faraday Soc.*, **30**, 168 (1934).

[13] Barnicoat, *Analyst*, **60**, 653 (1935).

and 0.009 mole per cent. of diacetyl were made up from (a) pure acetone, (b) products from acetone decomposed to 1.51% and (c) products from acetone decomposed to 9.53%. In all samples containing 0.025 mole per cent. diacetyl the characteristic red precipitate formed within twenty minutes after the solution had been made alkaline. In samples (a) and (c) containing 0.009 mole per cent. of diacetyl, the precipitate formed after standing overnight, but sample (b) containing 0.009% diacetyl gave no definite test. These experiments indicate that diacetyl in the products from the decomposition of acetone in amounts exceeding 0.025% could have been detected easily and probably could have been detected down to 0.009%.

To determine whether diacetyl in such low concentrations either accelerated the decomposition of acetone or eliminated the induction period at 506°, we made up solutions of liquid acetone containing 0.026 mole per cent. diacetyl and measured the rate of decomposition of vapor from this solution. Assuming the solution is ideal, a concentration of about 0.007% diacetyl was present in the gas phase. In another experiment a mixture of acetone and 0.055% diacetyl in the vapor phase was prepared in the mixing bulb. In the latter case there was a noticeable acceleration of the rate, and in both cases the acetone started to decompose immediately; but the pressure–time curves were concave upward, just as with pure acetone. Since the addition of 0.055% diacetyl, which is larger than the amount which could have been present in the acetone decomposition, failed to alter the shape of the pressure–time curve, it appears that the induction period is due to the building up of some intermediate other than diacetyl.

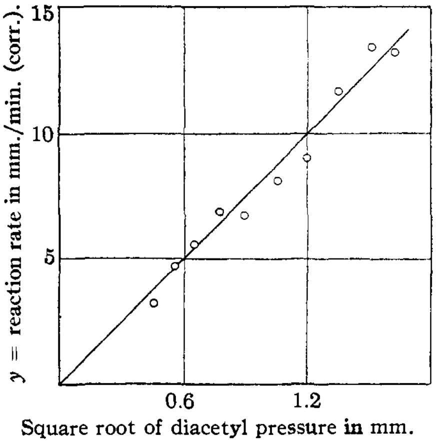

Fig. 2.—Decomposition of acetone in presence of varying amounts of diacetyl: temp. 526°. acetone pressure, approximately 200 mm.

In view of the previously mentioned experimental results it is probable that the promoting effect of diacetyl is caused by the radicals which it produces. In some cases the absence of an appreciable promoting effect on acetone using compounds other than diacetyl may be due to the fact that the radicals are formed and then destroyed before the acetone vapor has reached a temperature where a chain decomposition can occur. In other cases a compound may have no appreciable effect because it does not produce a sufficient concentration of free radicals.

Assuming that the following reactions are occuring in the promoted decomposition

$$\begin{aligned} CH_3COCOCH_3 &\longrightarrow 2CH_3 + 2CO && (1)\\ CH_3COCH_3 &\longrightarrow 2CH_3 + CO && (2)\\ CH_3 + CH_3COCH_3 &\longrightarrow CH_4 + CH_2COCH_3 && (3)\\ CH_3COCH_2 &\longrightarrow CH_3 + CH_2{=}CO && (4)\\ CH_3 + CH_2COCH_3 &\longrightarrow CH_3CH_2COCH_3 && (5) \end{aligned}$$

reactions (1) and (2) represent several steps involving the formation and decomposition of radicals more unstable than methyl. Reactions (2) to (5) represent the chain mechanism for the decomposition of acetone,[14] which has received support from the fact that the addition of propylene retards the decomposition of acetone.[7]

From this mechanism, if the chain length is ten or greater, the rate of decomposition can be expressed as

$$\frac{-\mathrm{d}M_2}{\mathrm{d}t} \cong \left(\frac{k_1k_3k_4M_1M_2}{k_5} + \frac{k_2k_3k_4M_2^2}{k_5}\right)^{1/2} \qquad \text{(I)}$$

where M_1 is $CH_3COCOCH_3$ and M_2 is CH_3COCH_3. Let $z = -\mathrm{d}M_2/\mathrm{d}t$, the rate of the promoted decomposition, $x = (k_2k_3k_4/k_5)^{1/2}M_2$, which is the rate of the unpromoted decomposition, and $y = (k_1k_3k_4M_1M_2/k_5)^{1/2}$, then the following expression is obtained from (I)

$$z = (y^2 + x^2)^{1/2}$$

Since z and x can be measured, y can be calculated. For a given temperature and acetone pressure, y should vary as the square root of the diacetyl concentration. In Fig. 2 values of y, which were obtained from runs at 526° at approximately 200 mm. pressure using the initial rates of pressure increase shown in Table I, are plotted against the square root of the diacetyl pressure. Considering the limits of experimental error, a fairly satisfactory agreement is obtained. Moreover, for the

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(14) Rice and Herzfeld, This Journal, 56, 284 (1934).

promoted reaction where x^2 is small compared to y^2, the dependence of the initial rate on the acetone pressure is in the neighborhood of a 0.5 power, as would be expected from the above expression. In addition, since the pressures of diacetyl and acetone in these experiments are known, a comparison of the values of x and y indicates that k_1 is larger than k_2 by a factor of 4×10^3.

Diethyl Ether.[15]—In a series of four experiments it was found that the initial rate of the decomposition at 499° for samples of diethyl ether at 190 mm. containing 1% diacetyl is four times that of pure diethyl ether. The pressure increase after eight minutes for diethyl ether with 1% diacetyl was about 72%, while for diethyl ether alone the pressure increase was 19%.

Acetaldehyde.—Addition of 0.9% diacetyl to 205 mm. of acetaldehyde increases the initial rate of decomposition at 499° by a factor of six. The pressure increase after four minutes amounted to 58%, and under the same conditions the decomposition of pure acetaldehyde gave a pressure increase of 15%. In contrast to the results with acetone, the effect of diacetyl on acetaldehyde as well as diethyl ether persists over practically the entire decomposition.

Ethylene.—In addition to promoting the chain decompositions of compounds such as ethers and aldehydes, free radicals have been found to accelerate the polymerization of ethylene.[3c,16] Therefore, the influence of diacetyl on the rate of polymerization of ethylene was investigated. The results are summarized in Table III, in which P_{30-0} indicates the pressure decrease after thirty minutes. It is evident that the addition of diacetyl does increase the rate of polymerization.

TABLE III

POLYMERIZATION OF ETHYLENE AT 450°

P_0, mm.	Diacetyl, %	$-(dP/dt)_0$, mm./min.	P_{30-0}, mm.
689	0.0	0.54	16.1
687	1.14	4.0	60.1
696	0.0	0.61	18.5
688	1.11	4.2	59.9

Ethyl Alcohol.—In a number of studies[17] it has been shown that the thermal decomposition of ethyl alcohol involves both the dehydration to ethylene and dehydrogenation to acetaldehyde. The latter reaction, which is the more important of the two, is followed by the decomposition of acetaldehyde into methane and carbon monoxide. Although ethyl alcohol can be decomposed to produce free radicals,[18] no free radical mechanism has been proposed for the ordinary decomposition. However, the data from experiments with ethyl alcohol containing diacetyl, given in Table IV, show that a promoted chain decomposition can occur. The fact that the pressure increases for the ordinary and the promoted decompositions were essentially the same, amounting to 154 and 160%, respectively, is an indication that probably the same over-all reactions are occurring. Since, even in glass vessels, some heterogeneous reaction does take place, experiments were made using a packed vessel with the surface to volume ratio increased by a factor of eighteen. The rate of decomposition was increased about 2.5 times that of pure ethyl alcohol, indicating that about 10% of the reaction occurring in the unpacked vessel was heterogeneous. However, the rate of decomposition in the packed vessel with added diacetyl was somewhat slower than the promoted decomposition in the unpacked vessel. Since the over-all pressure increases in the packed and unpacked vessels are approximately equal, the results are probably not due to any change in the type of reaction. These experiments, therefore, point to the fact that the chain decomposition which diacetyl promotes is a gas phase reaction.

TABLE IV

DECOMPOSITION OF ETHYL ALCOHOL AT 540°

P_0, mm.	Diacetyl, %	$t_{1/4}$, min.	$t_{1/2}$, min.
44	0.0	10.3	25.9[a]
39	1.27	1.69	6.9[a]
38	2.53	1.37	4.5[a]
Packed bulb. $S/V_{\text{packed}} \div S/V_{\text{unpacked}} = 18$			
44	0.0	4.0	11.3[a]
43	2.49	1.78	8.5
43	2.74	1.54	7.6

[a] Average of two or more runs.

Summary

In the temperature range 506–540° the decomposition of acetone is accelerated by the addition of small amounts of diacetyl. The acceleration of the decomposition results in an increased rate of

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(15) In this Laboratory (J. H. U.) Mr. F. C. Kelton has found that the presence of 0.4% of diacetyl increases the rate of decomposition of 360 mm. of dimethyl ether at 483° fourfold and that the addition of propylene inhibits about 90% of the promoted decomposition.

(16) Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930); O. K. Rice and Sickman, *ibid.*, **57**, 1384 (1935).

(17) Ipatiew, *Ber.*, **34**, 3579 (1901); **36**, 1993 (1903); Peytral, *Bull. soc. chim.*, **27**, 34 (1920).

(18) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932)

formation of ketene. A chain mechanism, which accounts for the pressure dependence of the reaction, has been proposed.

Diacetyl also promotes the decompositions of diethyl ether, acetaldehyde, and ethyl alcohol, as well as the polymerization of ethylene.

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RECEIVED FEBRUARY 13, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of HCO_3^- from 0 to 50°

BY HERBERT S. HARNED AND SAMUEL R. SCHOLES, JR.[1]

The cell

$$H_2 \mid Na_2CO_3(m_1).\ NaHCO_3\ (m_2),\ NaCl\ (m_3) \mid AgCl - Ag$$

has been employed by MacInnes and Belcher[2] to determine the ionization constant of HCO_3^- at 25 and 38°. These measurements have been extended by us to include the range from 0 to 50° and sufficient measurements obtained at intermediate temperatures to determine the entropy, heat content and heat capacity of the ionization reaction.

Experimental Technique and Observed Electromotive Forces

An important feature of this investigation is the use of a stationary cell connected to an enclosed gas pumping system. By this device. the hydrogen circulates through the cell unidirectionally, flowing through a saturator. then over the hydrogen electrode. and finally out of the cell back into the gas pump. This is effected by a suitable set of electrically controlled valves.[3] By means of this enclosed gas system. it is possible to sample the gas for analysis at any time. or if possible determine its composition by thermal analysis. Therefore. a cell of this kind is very well adapted for measurements in which small quantities of gas (300 cc.) are available. when the composition of the gas is required or when the solvent itself is highly volatile. In the latter case. only a short hydrogen saturation device is required.

The behavior of the cells was quite satisfactory. It was possible to change the temperature from 25 to 50° or from 25 to 0° and then back to 25° and reproduce the readings to within 0.1 mv. Two complete series of results were obtained. Of these. the second was the more consistent. We attribute this to the improvement in technique acquired as a result of experience. Duplicate measurements were made at each concentration and the recorded observations represent the mean of these results.

The solutions were made by introducing one-half an equivalent of a standard hydrochloric acid solution to a standard sodium carbonate solution whereby the carbonate. acid carbonate and chloride were present in nearly a 1:1:1 ratio. The acid was added very carefully drop by drop in order to avoid loss of carbon dioxide by local action. The concentrations of electrolytes were known to be within 0.1%. No correction was necessary for the very small partial pressure of carbon dioxide over these solutions.[4]

Since the final values of the ionization constant were evaluated from our second series of results, only these have been recorded in Table I. The first series of results, however, were fairly good and will be shown on the figures. The accuracy of these measurements is estimated to be about 0.1 mv. Some results were obtained at lower ionic strengths but it was found that when the chloride concentration was below 0.003, or the total ionic strength below 0.018, less consistent results were obtained. This concords with our previous experience with cells of this type.

Calculation of Ionization Constant.—By combining the equation of the cell

$$E = E^0 - RT/F \ln m_{H}m_{Cl}\gamma_{H}\gamma_{Cl} \qquad (1)$$

with the thermodynamic equation for the reaction namely

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

$$K_{2A} = \frac{m_{H}m_{CO_3}\gamma_{H}\gamma_{CO_3}}{m_{HCO_3}\gamma_{HCO_3}} \qquad (2)$$

we obtain

$$(E - E^0)k + \log \frac{m_{HCO_3}m_{Cl}}{m_{CO_3}} + \log \frac{\gamma_{HCO_3}\gamma_{Cl}}{\gamma_{CO_3}} = - \log K'_{2A} = - \log K_{2A}]_{\mu = 0} \qquad (3)$$

E^0 is the standard potential of the cell: $H_2 \mid HCl\ (m) \mid AgCl - Ag$, $k = F/2.3026\ RT$, and m_{HCO_3}, γ_{HCO_3}, etc., are the molalities and activity coefficients of the ionic species designated by subscripts. K_2' is an apparent ionization constant which equals the true ionization constant at zero ionic strength.

Two methods of extrapolation have been employed. The first method, employed by MacInnes and Belcher, is to combine the term con-

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(1) This communication contains part of the material of a dissertation presented by Samuel R. Scholes, Jr., to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1940.

(2) MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933); **57**, 1683 (1935).

(3) A complete description of the apparatus is contained in the Dissertation to which reference has been made.[1]

(4) Walker, Bray and Johnston, THIS JOURNAL, **49**, 1935 (1927).