obtained with mixtures of the pure oxides are of interest.[10]

Table II

Wt. % oxide (added)		
CuO	Cu_2O	Wt. % Cu_2O (found)
39.8	60.2	60.7
65.5	34.5	34.9
92.0	8.0	7.9

It is evident from a study of the above reactions that although Karl Fischer reagent is a less specific reagent for water in inorganic analysis than in the organic field, this circumstance is not wholly prejudicial. The great majority of interfering compounds follow relatively simple stoichiometric reaction patterns, thus permitting the use of the reagent for the quantitative determination of a variety of inorganic substances.

Summary

1. The nature and stoichiometry of reactions of Karl Fischer reagent with inorganic substances other than water have been investigated.

2. Two distinct classes of reactions have been described: (a) reactions involving the oxygen of metal oxides or salts of oxygen acids, and (b) oxidation or reduction of cations and anions by a modified iodine–iodide couple. A number of examples are given.

Wilmington, Delaware Received July 24, 1941

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[10] Since microcrystalline oxides occurring as minerals are often much less soluble than some of the less dense synthetic products, selected crystals of cuprite (Cu_2O), pyrolusite (MnO_2 + 2% H_2O) and zincite (ZnO) were ground to pass through a 200-mesh screen and were then analyzed by means of the reagent. Cuprite reacted completely in two hours; pyrolusite required six hours with shaking but reacted completely. The zincite although of good external appearance never exceeded 80% of the theoretical reaction even after forty-eight hours, hence was probably heavily contaminated.

[Contribution from the Physiological Laboratory of Cambridge University]

The Kinetics and Rapid Thermochemistry of Carbonic Acid

By F. J. W. Roughton

In 1924 Hartridge and Roughton[1] developed a method for following the time course of the heat effects in rapid chemical changes. Our method was to drive the two solutions, whose reaction was to be studied, through separate leads into a mixing chamber and thence into an observation tube. The temperature of the running fluid at several known distances from the mixing chamber was measured thermo-electrically, and from these readings together with the speed of fluid flow down the observation tube the temperature change could be plotted against the time of the reaction. Subsequent work[2,3,4] led finally to an improved technique by which it was possible to follow, to within 1–2%, the time course of heat effects over a period of 0 to 0.01 second even when the total temperature change was no greater than 0.01°.

In the present paper I have applied the technique of Bateman and Roughton to the study of the rapid thermochemistry and kinetics of formation of carbon dioxide from bicarbonate by mixture with acid. This is usually supposed to go in two stages, of which the first

$$H^+ + HCO_3^- \longrightarrow H_2CO_3 \qquad (1)$$

should be practically instantaneous, like all similar ionic reactions in water (see Roughton, ref. 2) whereas the second

$$H_2CO_3 \longrightarrow CO_2 + H_2O \qquad (2)$$

has a definite time course, being a molecular reaction. The present research not only confirms the two-stage theory directly, but also yields for the first time the separate heats of reactions (1) and (2), the previous methods of calorimetry having given only the sum of these two heats. In addition, the velocity constant of reaction (2), *viz.*, k_0, is obtained over the range 0–37°. No direct measurements of k_0 at mammalian body temperature were hitherto available; this was an important gap in view of the role of reaction (2) in controlling the speed of elimination of carbon dioxide in the expired air.

Experimental

Preparation of Reagents

Hydrochloric Acid Solutions.—0.03 to 0.12 *N* by dilution of concd. hydrochloric acid, the final titer being determined by standard alkali.

Sodium Bicarbonate Solutions.—0.03 to 0.1 *M* by dissolving weighed amounts of sodium bicarbonate in 5 liters water and shaking the solution in a 10-liter bottle with air containing 5% carbon dioxide so as to reduce the carbonate ion content to less than 1% of the bicarbonate ion content, thus practically eliminating subsequent heat effects

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(1) Hartridge and Roughton, *Proc. Cambridge Phil. Soc.*, **22**, 426 (1924).

(2) Roughton, *Proc. Roy. Soc.* (London), **A104**, 376 (1930).

(3) La Mer and Read, This Journal, **52**, 3098 (1930).

(4) Bateman and Roughton, *Biochem. J.*, **29**, 2622 (1935).

due to the combination of H^+ with $CO_3^=$ ions. The sodium bicarbonate was determined by titration with standard hydrochloric acid using brom cresol green as indicator.

Simplification of Bateman and Roughton's Procedure.—The only improvement since 1935 has been the use of a combined differential-absolute thermocouple. This consists of a length of 24-gage enamelled constantan wire (30 to 40 cm.) to the two ends of which (Θ, Θ_s) are soldered separate lengths of 32-gage copper wire. A third length of 32-gage enamelled copper wire is soldered to a point (Θ') 3 cm. distant from Θ. Θ and Θ' are placed in the observation tube of the rapid reaction apparatus and Θ_s is placed in a standard constant temperature (within 0.005° of the thermostat surrounding the whole apparatus). Θ, Θ' and Θ_s are connected to the terminals of a six-point double-throw switch so that either Θ and Θ' (differential thermocouple) or Θ and Θ_s (absolute thermocouple) can be connected with the measuring galvanometer. In this way the difference of temperature between two points in the running fluid or the actual temperature of a single point can be determined merely by adjusting Θ-Θ' to the appropriate position in the observation tube. The whole experiment can thereby be carried through with less fluid, but with more speed and accuracy than in Bateman and Roughton's method.

In other respects Bateman and Roughton's procedure was followed exactly, the temperature rise due to the chemical reaction usually being determined at 2, 5, 8 and 11 cm. from the orifice of the mixing chamber.

The proportions of hydrochloric acid and sodium bicarbonate in the mixed fluid were calculated from the titer of the latter and the respective titers of the hydrochloric acid and the sodium bicarbonate before mixture.

Experimental Results

Figure 1 shows the results of a typical experiment in which 0.0587 *M* hydrochloric acid was mixed with 0.0386 *M* sodium bicarbonate at 17.85° and the temperature rise determined at points distant, respectively, 2, 5, 8 and 11 cm. from the orifice of the mixing chamber. The heat evolution is seen to occur in two phases: the first, a rapid one involving a rise of temperature of 0.023°, is due solely to reaction (1), *viz.*, $H^+ + HCO_3^- \rightarrow H_2CO_3$, which, as it belongs to the class of simple ionic reactions, must be complete as soon as mixing is complete (see Roughton[2]). The second, relatively slow, phase, lasting up to one second, is due to reaction (2), *viz.*, $H_2CO_3 \rightarrow CO_2 + H_2O$, which, being molecular, has a definite time course. The first method of calculation is as follows. Let

k_0 = velocity constant of the reaction $H_2CO_3 \rightarrow CO_2 + H_2O$

ΔH_1 = heat of reaction $H^+ + HCO_3^- \rightarrow H_2CO_3$ (not previously known)

ΔH_2 = heat of reaction $H_2CO_3 \rightarrow CO_2 + H_2O$ (not previously known)

$\Delta H_1 + \Delta H_2$ = total heat of reaction $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$

For this last reaction values in the range 0–40° are given by Shedlovsky and MacInnes[5]

$\Theta_2, \Theta_5, \Theta_8, \Theta_{11}$ = respective temperature rises of the running fluid at corresponding points of the observation tube

t_2, t_5, t_8, t_{11} = times from completion of mixing

Θ_0 = temperature rise of the reacting fluid after mixture is first complete. This can be obtained by extrapolating the slow phase of the curve in Fig. 1 back to $t = 0$, or preferably by calculation (*vide infra*)

Θ_∞ = temperature rise of the fluid when all reactions in it are complete. This is calculated from ($\Delta H_1 + \Delta H_2$) and the composition of the mixed fluid

Then $\Theta_\infty - \Theta_0$ = temperature rise due to the reaction $H_2CO_3 \rightarrow CO_2 + H_2O$. Since the reaction is unimolecular

$$(\Theta_\infty - \Theta_0) = (\Theta_\infty - \Theta_2)e^{k_0t_2} = (\Theta_\infty - \Theta_5)e^{k_0t_5} = (\Theta_\infty - \Theta_8)e^{k_0t_8} = (\Theta_\infty - \Theta_{11})e^{k_0t_{11}} \quad (3)$$

Therefore

$$\log_e \frac{\Theta_\infty - \Theta_2}{\Theta_\infty - \Theta_5} = k_0(t_5 - t_2)$$
$$\log_e \frac{\Theta_\infty - \Theta_5}{\Theta_\infty - \Theta_8} = k_0(t_8 - t_5)$$
$$\log_e \frac{\Theta_\infty - \Theta_8}{\Theta_\infty - \Theta_{11}} = k_0(t_{11} - t_8) \quad (4)$$

Θ_∞ having been calculated as above, and Θ_2, t_2, etc., measured in the experiment, solution of (4)

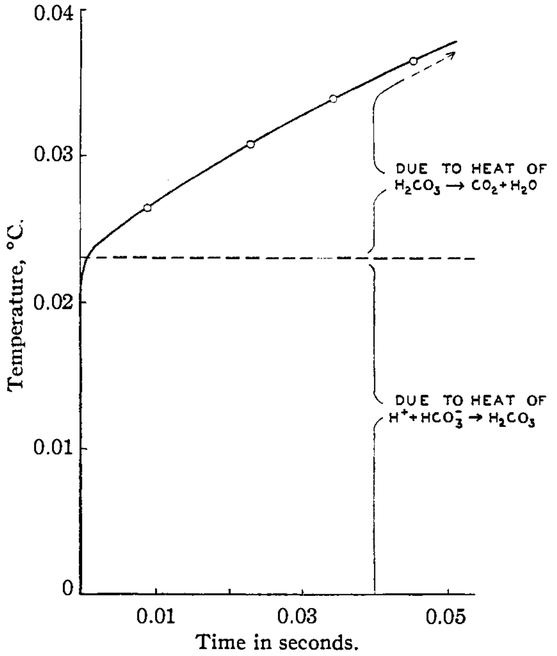

Fig. 1.—Typical experiment showing two stages in evolution of heat when hydrochloric acid is mixed with sodium bicarbonate.

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[5] Shedlovsky and MacInnes, THIS JOURNAL, **57**, 1705 (1935).

TABLE I

Temp., °C.	Reagents R (M NaHCO$_3$)	Reagents L (M HCl)		k_0, moles/liter per sec.	ΔH_1 in cal.	ΔH_2 in cal.	$\Delta H_1 + \Delta H_2$ (from present data)	$\Delta H_1 + \Delta H_2$ (Shedlovsky and MacInnes)[5]
0.0	0.038	0.059		2.06	1605	2880		
.0	.040	.060		1.89	1820	2665		
			Av.	1.97	1710	2775		**4485**
17.7	.079	.059		13.8	1315	1345		
17.8	.040	.060		14.6	1205	1455		
18.0	.040	.115		15.4	1200	1460		
			Av.	14.6	1240	1420		**2660**
27.1	.057	.039		29.0	1130	890	2020	
27.0	.061	.042		31.2	1070	1080	2150	
26.9	.062	.042		34.5	750	1050	1800	
27.0	.061	.041		29.4	900	1120	2020	
			Av.	31.0	960	1040	2000	1930
36.55	.038	.059		87.0	650	460	1110	
36.80	.042	.060		73.0	725	435	1160	
			Av.	80.0	685	450	1140	1210

gives directly three values of k_0. The mean of these when substituted in (3) enables Θ_0 to be calculated, and thence ΔH_1. Subtraction of ΔH_1 from Shedlovsky and MacInnes' value of $\Delta H_1 + \Delta H_2$ gives ΔH_2.

In the experiment plotted in Fig. 1

$\Delta H_1 + \Delta H_2 = 2660$ cal. at 17.85°
Final carbon dioxide content of mixed fluid = 0.0192 M
Therefore $\Theta_\infty = 2660 \times 0.0192 \times 10^{-3} = 0.051°$
$k_0 = 14.2, 14.6, 15.0$ from (4); mean = 14.6 at 17.85°
Θ_0 from (3) = 0.023°
whence $\Delta H_1 = 1205$ cal., $\Delta H_2 = 1455$ cal. at 17.85°

This method of calculation has been used for all the data at 0 and 18° given in Table I, which shows that k_0 is independent of variations in the concentration of sodium bicarbonate and hydrochloric acid and *p*H.

Table I also gives data at 27 and 37°; in this higher temperature range the reaction $H_2CO_3 \rightarrow CO_2 + H_2O$ proceeds far enough within the space of the observation tube for k_0, Θ_0 and Θ_∞ all to be calculated by a second method which does not require independent knowledge of Θ_∞. For from 3 it follows that

$$(\Theta_2 - \Theta_5)/(\Theta_5 - \Theta_8) = (e^{-k_0t_2} - e^{-k_0t_5})/(e^{-k_0t_5} - e^{-k_0t_8})$$

and

$$(\Theta_5 - \Theta_8)/(\Theta_8 - \Theta_{11}) = (e^{-k_0t_5} - e^{-k_0t_8})/(e^{-k_0t_8} - e^{-k_0t_{11}}) \quad (5)$$

The values of $(\Theta_2 - \Theta_5)/(\Theta_5 - \Theta_8)$ and of $(\Theta_5 - \Theta_8)/(\Theta_8 - \Theta_{11})$ were obtained directly from the differential thermocouple readings and being appreciably greater than 1.0, enabled values of k_0 to be calculated from (5) with fair precision, since the values of t_2, t_5, t_8 and t_{11} were also known.

From the value of k_0 so obtained and the differential reading in the 2–5 position which gave

$$(\Theta_5 - \Theta_2) = (\Theta_\infty - \Theta_0)(e^{-k_0t_5} - e^{-k_0t_2}) \quad (6)$$

the value of $\Theta_\infty - \Theta_0$ was obtained and thence by equation (3) Θ_0 and Θ_∞ separately. In this way the values of ΔH_1, ΔH_2 and $(\Delta H_1 + \Delta H_2)$ were all obtained independently of previous data. Table I shows that the values of $\Delta H_1 + \Delta H_2$ thus determined at 27 and 37° agree within experimental error with the values given by Shedlovsky and MacInnes.

General Accuracy and Comparison with Previous Data.—Table II summarizes the values of k_0 at 18° as determined previously by several diverse methods, some of which were only very rough. The actual values were determined over the range 14–20°, and corrected to the standard

TABLE II

PREVIOUS VALUES OF k_0 AT 18°

Author	Method	k_0
Faurholt[6]	Conversion of carbon dioxide into carbamate	16.3
Saal[7]	Rapid flow—hydrogen electrode	12.8
Saal[7]	Rapid flow—conductivity	10.2
Brinkman, Margaria and Roughton[8]	Rapid flow—photoelectric	13.6
	Rapid flow—aerotonometric	17.0
Roughton[9]	Thermoelectric (mean of earlier rough results by present technique)	14.0
	General average	14.0

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(6) Faurholt, *J. chim. phys.*, **21**, 400 (1924).

(7) Saal, *Rec. trav. chim.*, **47**, 264 (1928).

(8) Brinkman, Margaria and Roughton, *Phil. Trans. Roy. Soc.* **A232**, 65 (1933).

(9) Roughton, *J. Biol. Chem.*, **30**, lxxxvi (1936).

temperature of 18° by means of the temperature coefficient given by the data of Table I.

The figures vary over an uncomfortably wide range, but their general average, *viz.*, 14.0, agrees satisfactorily with the figure of 14.6 in Table I, which may be taken as correct to ±5%. The same accuracy may be claimed for the value of k_0 at 27°, but the values at 0 and 37° are probably accurate only to ±10%, because of the greater difficulty of obtaining satisfactory results at temperatures differing by more than 10° from room temperature. The general accuracy is, on the whole, up to that attained in previous researches by the rapid flow methods.

Effect of Temperature on k_0.—The average energy of activation over the range 0–37° is found to be 16,500 cal., though the actual plot of log k_0 against $1/T$ shows a small decrease with rise of temperature, too slight, however, to be determined from values of k_0 accurate only to 5–10%. Such a decline is in line with the trend of ΔH_2 which drops from 2800 cal. at 0° to 450 cal. at 37°.

Effect of Temperature on ΔH_1.—Harned, *et al.*,[10] have studied exhaustively the effect of temperature on the ionization constant of many weak acids. Their results were first fitted by the approximate formula

$$\log K_1 = \log K_{\text{max.}} - 5 \times 10^{-5}(t - \Theta)^2 \qquad (7)$$

Θ being the temperature corresponding to the maximum value of K. Later this was generalized to

$$\log K_1 = \log K_{\text{max.}} - p(t - \Theta)^2 \qquad (8)$$

p being a constant characteristic for each acid. Equations (7) and (8) lead, respectively, to values of ΔH_1 as follows

$$\Delta H_1 = -2.3 \times 10^{-4} RT^2(t - \Theta) \qquad (9)$$

and

$$\Delta H_1 = -4.6pRT^2(t - \Theta) \qquad (10)$$

Other expressions for ΔH_1 are

$$\Delta H_1 = A - BT - DT^2, \text{ giving } -RT \ln K = A + BT \ln T - CT + DT^2 \qquad (11)$$

$$\Delta H_1 = A - BT, \text{ giving } -RT \ln K = A + BT \ln T - CT \qquad (12)$$

$$\Delta H_1 = A - DT^2, \text{ giving } -RT \ln K = A - CT + DT \qquad (13)$$

All these equations have been tested out recently by Harned and Robinson[10] on the values of the ionization constants of formic acid from 0 to 60°. Equations (11), (12) and (13) were found to fit the data within experimental error and equations (9) and (10) nearly so.

Since carbonic acid is the hydroxy acid of formic acid, it was of especial interest to see whether the values of ΔH_1 in Table I could be fitted by the equations given by Harned and Robinson. It was found that all five equations fitted the data for various temperatures within experimental error (±70 cal.) and that the maximum value of K_1 should occur at about 55°.

The Equilibrium Constant, K, of the Reaction $CO_2 + H_2O \rightleftarrows H_2CO_3$.—

$$K = [CO_2]/[H_2CO_3] = k_0/k_u \qquad (14)$$

where k_u = the velocity constant of the reaction $CO_2 + H_2O \rightarrow H_2CO_3$ = 0.0021 at 0°[11,12,13] (previous values of k_u are too high owing to failure to allow for the catalytic effect of buffers on the reaction). Therefore $K = 2.0/2.1 \times 10^{-3} = 950$ at 0°.

Values at other temperatures can be calculated therefrom thermodynamically with the aid of the values of ΔH_2 in Table I. This, however, will be deferred until accurate values of k_u at temperatures other than 0° are available.

The True First Ionization Constant, K_1, of Carbonic Acid.—

$$K_1 = a_{H}a_{HCO_3}/[H_2CO_3] \qquad (15)$$

where a_H, a_{HCO_3} are the activity coefficients of the corresponding ions. Experiments on the rate of CO_2 formation in bicarbonate–cacodylate buffer mixtures, pH 5.5 to 7.0, give k_0/K_1.[8] In recent experiments at 0° I have found by Roughton and Booth's[11] manometric method, that when the catalytic effect of the cacodylate ion is allowed for

$$k_0/K_1 = 8000 \text{ at } 0°$$

Therefore $K_1 = 2.0/8000 = 2.5 \times 10^{-4} \pm 0.3 \times 10^{-4}$. This value agrees fairly well with previous rough values, *e. g.*, Brinkman, Margaria and Roughton found by the rapid flow optical method that $K_1 = 2.4\ (\pm 0.4) \times 10^{-4}$ at 15°, which from the heat data of Table I indicates that $K_1 = 2.05\ (\pm 0.4) \times 10^{-4}$ at 0°.

Carbamic Acid, NH_2COOH.—This substance is generally considered to be too unstable to exist in the free state though the salts—the carbamates—are stable in the solid form, and only decompose slowly in alkaline solution. In some preliminary experiments by the present technique, in which ammonium carbamate was mixed with hydrochloric acid, it was found that the velocity

[10] Harned and Embree, THIS JOURNAL, **56**, 1050 (1934); Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

[11] Roughton and Booth, *Biochem. J.*, **32**, 2049 (1938).

[12] Hastings and Kiese, *J. Biol. Chem.*, **132**, 267 (1940).

[13] Mills and Urey, THIS JOURNAL, **62**, 1019 (1940).

constant for the decomposition of free carbamic acid was about 80 at 0°, thus corresponding to a half-life of about 0.009 sec. The ionization constant of the carboxyl group was calculated roughly by the method used above for K_1 and found to be about 1.8×10^{-6} at 0°. No indication was found either of combination of a second H^+ ion with the $-NH_2$ group in very acid solution, or of zwitterion formation by the NH_2COOH molecule like that found in glycine or other amino acids. Further discussion must be postponed until fuller data are available, but owing to present conditions the writer will be unable to undertake such work for some time.

Summary

The rate of heat evolution when hydrochloric acid is mixed with sodium bicarbonate has been studied by the thermal method of measuring the velocity of rapid chemical reactions. The heat was found to be evolved in two stages, of which the first was practically instantaneous, being due to the combination of H^+ and HCO_3^- ions to form H_2CO_3, whereas the second slower stage lasting up to one second was due to the dissociation of H_2CO_3 into CO_2 and H_2O.

The data gave values for the dissociation velocity constant of H_2CO_3, and for the separate heats of the two reactions over the range 0–40° instead of the *sum* of the two heats as hitherto measured by the ordinary calorimetric methods. The heat of the reaction $H^+ + HCO_3^-$ was found to vary with temperature in the manner characteristic of weak acids, as studied by Harned.

The "true" first ionization constant of carbonic acid was calculated independently from the present data and checked fairly well with certain previous values.

Preliminary measurements were also made of the rate of dissociation of free carbamic acid, and of the ionization constant of its carboxyl group.

CAMBRIDGE, ENG. RECEIVED AUGUST 6, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Alkali and Alkaline Earth Metals as Catalysts in the Hydrogenation of Organic Compounds

BY F. W. BERGSTROM AND JOHN F. CARSON

Hugel and Friess[1] and Hugel and Gidaley[2] have hydrogenated a number of organic compounds with sodium hydride and high pressure hydrogen. Thus, stilbene and 1,4-diphenylbutadiene were hydrogenated to dibenzyl and 1,4-diphenylbutane, respectively, while anthracene was hydrogenated successively to 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene and finally to octahydroanthracene.

As a result of this work, Hugel and Gidaley[2] showed that only those compounds capable of adding sodium metal could be reduced by sodium hydride and hydrogen. This suggests several possibilities for the mechanism of the reaction. The sodium hydride may dissociate reversibly into sodium and hydrogen, the former may add to the double bond and then be split off and replaced by hydrogen by a process that has been termed hydrogenolysis.[3] The sodium hydride may itself add to the double bond, the sodium then being replaced as above by hydrogen or, finally, the sodium hydride may simply act as a contact catalyst in the usual sense.

In the present work we have attempted to answer the question of the mechanism of this reaction by reducing organic compounds with high pressure hydrogen in the presence of alkali metals as catalysts. In order to see whether the alkali metals are specific catalysts for the reaction, we also have examined the activity of calcium.

Experimental

All hydrogenations were carried out in a high pressure rocking autoclave manufactured by the American Instrument Company. A stainless steel liner was used, the capacity of the bomb containing the liner being about 950 cc. In general, the initial hydrogen pressures were from 1000 to 2000 lb./sq. in. and the temperatures varied between 130 and 270°. Below 200° the catalysts were relatively inactive, except toward pyridine. Sodium, potassium and lithium, of the highest commercial purity, were cut and weighed under benzene before being transferred to the bomb. Calcium was activated by two methods: (1) the metal was pulverized under benzene in a stainless steel ball mill with stainless steel balls. This treatment produces a

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[1] Hugel and Friess, *Bull. soc. chim.*, **49**, 1042 (1931).

[2] Hugel and Gidaley, *ibid.*, **51**, 639–644 (1932).

[3] Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 416.