of the data warrant. We feel confident that some of the data at 30° must be in error.

It is of interest to note that in Krapivin's data at 0.01 N the addition of 0.01 N sodium bromide, iodide or nitrate produced identical effects, as did the further addition of 0.01 N bromo-acetate, *i. e.*, k increased from 0.455 to 0.502–0.505. This is in agreement with the principle of specific interaction, (see ref. 7b). On the other hand, addition of 0.01 N sodium thiosulfate gave a value of $k = 0.504$, while 0.01 N sodium sulfate increased k to 0.516, even though the ionic strength is the same as in the presence of sodium thiosulfate.

Our experiments are being continued from the standpoint of specific salt effects and the effect of the relative position of the charge and the bromine atom upon the velocity.

The assistance given by Mr. R. W. Fessenden is gratefully acknowledged.

Summary and Conclusions

The velocity data of the reaction $BrCH_2COO^- + S_2O_3^{--} \longrightarrow S_2O_3\text{-}CH_2COO^{--} + Br^-$ studied by Krapivin for the sodium salts at moderate dilutions have been extended from 0.01 N to 0.0005 N. The data strongly support Brönsted's theory of reaction velocity. In the presence of sodium ions the limiting slope predicted from the Debye theory holds from 0.001 N (0.0025μ) down to the lowest concentration studied. At higher concentrations the slope falls off, reaching a value of one-fourth the theoretical value at 0.35μ. The experiments are being continued.

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NOTES

A Simple Laboratory Vacuum Regulator.—Among various methods of maintaining a constant temperature in the range from room temperature to nearly red heat, the vapor-bath with boiling liquid under constant, automatically controlled, reduced pressure is perhaps the most convenient and satisfactory. The device described in this note for controlling the degree of vacuum and thus the temperature is not new in principle, but its simplicity and utility make it available to any chemical laboratory. A device based upon similar principles has recently been described.[1] The chief difference between the two devices consists in the use of a glass stopcock in the present instance instead of the combination of a rubber stopper and capillary tube to control the ingress of air.

The essential features of the apparatus are shown in Fig. 1. The mercury in the manometer AA′ is adjusted by means of the leveling bottle F to such a position that when contact is broken with the platinum wire sealed into the closed arm A, the height h corresponds to the degree of

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[1] S. P. Miller and P. V. McKinney, *Ind. Eng. Chem.*, **20**, 552 (1928).

vacuum desired. Upon closing the electrical switch S, current flows from a 6-volt storage battery through the magnet coils of an ordinary doorbell buzzer, the terminals of which are connected directly to the binding posts so that the vibrator operates like the armature of a relay. The extended armature is attached at right angles to an extension of the stopcock handle in such a way that magnetization of the coils closes the stopcock C, allowing gas to be withdrawn from the condenser E and boiling tube G by means of the service vacuum or any other suitable source of suction. When the pressure in the system falls below the height h, the electrical circuit is broken, the armature is released and the stopcock opens by spring action of the relay. The influx of the air then increases the pressure until the electrical circuit is again closed, when the cycle is repeated. The manometer AA′ is constructed of two wide tubes connected by a narrow tube to minimize surges.

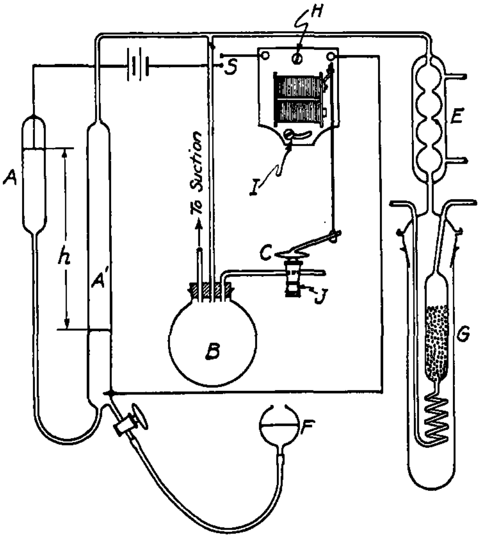

Fig. 1.

An essential feature of the automatically operated stopcock is the attachment of a short glass tube J to the small end of the stopcock barrel with de Khotinsky cement. This tube is slightly tapered and is fitted with a small cork which presses against the end of the stopcock plug to prevent the latter from settling tightly into the barrel. The stopcock is lubricated thoroughly with vaseline or a light stopcock grease. The stopcock handle may easily be extended by sealing a piece of 3-mm. diameter glass rod or tubing to it with de Khotinsky cement. A 3- or 4-liter flask B in the system serves as capacity to minimize surges. The pressure as observed on an open manometer attached to the system was constant to within less than 1 mm. of mercury at all pressures ranging from slightly less than atmospheric down to 1 cm. of mercury.

A slight adjustment of the degree of opening of the stopcock C is required for different pressures. This is accomplished by moving the relay about the screw H until the proper position with respect to the stopcock is found and then securing it in position by means of the screw I. The bore of the stopcock should be small, 1 mm. or less, so that only a slight movement entirely opens or closes it.

This device has been used continuously day and night for several months, interrupting the operation only over week ends, with only a very occasional failure, which has invariably been due to the battery running down. This device may readily be adapted to the control of vacuum distillations and other work in which a constant vacuum is desired.

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Automatic Cut-off Device for a Gas Fired Laboratory Mercury Still.—The distillation of mercury is an operation that is usually carried out in connection with other work and the still should therefore be so designed as to require the minimum of attention. The type of glass still described by Dennis,[1] with a ring type gas burner, gives excellent results but has the disadvantage that if care is not exercised to shut off the flame when the mercury gets low in the boiler, destruction of the still results. The sketch shows diagrammatically an automatic cut-off device which enables the operator to start the still and, except for an occasional filling, then go about other business and forget that it is going.

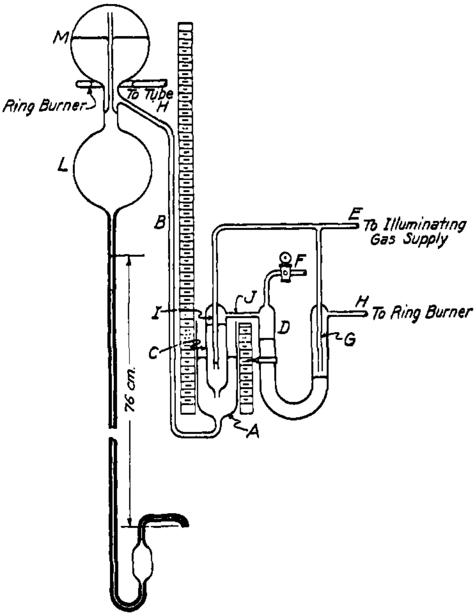

Fig. 1.

The still itself is the usual vacuum type, consisting of a boiling vessel M and condenser L with a 2-mm. bore capillary tube outlet of slightly greater length than the barometric column. Drops of mercury falling from the condenser into the capillary tube capture threads of gas ahead of them and thus maintain the high vacuum in the still by Sprengel pump action.[2] The mercury to be distilled is poured into the open tube A and flows through B into the still-head M. The flow stops when the difference between the

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[1] Dennis, "Gas Analysis," The Macmillan Company, New York, 1913, pp. 119–120.

[2] J. Wetzel, *Chem.-Ztg.*, **32**, 1228 (1908).

mercury levels in the still head and in A is equal to the prevailing barometric pressure less any slight pressure in the still. This difference in levels is maintained as the mercury distils, the level in A falling at the same rate as that in the still-head. Advantage is taken of this fact to operate the automatic cut-off device.

To start the still a slight suction is applied at F to displace the mercury in D, thus unsealing the tube G. The stopcock F is then closed so as to maintain this condition. Gas may now flow through EGH to the ring burner. The gas pressure is also communicated to I, which is immersed in the mercury in the filling tube A. As distillation proceeds, the mercury levels in M, A, C and I gradually fall until the effective seal on the tube I becomes less than that of the gas pressure within I. Gas then escapes through the mercury seal into CJD. The mercury in the U-tube is thus displaced so as to seal the open end of tube G and stop the gas flow to the burner. The tube C is extended below the open end of I sufficiently to prevent gas bubbling out through the mercury in A when the still-head cools.

The entire cut-off device is mounted to the frame carrying the still by means of a clamp (not shown) and is connected through H to the ring burner and through E to the gas supply by means of rubber tubing. The device may therefore be moved up or down to vary the depth of immersion of the tube C in the mercury in A. The depth of immersion is so adjusted that sufficient mercury remains in the still-head at the time of cut-off to cover the glass surface exposed to the flame. The level of the mercury in the still will, with a given setting of the device, vary with the mercury vapor pressure in the still-head and with the barometric pressure. The former may be held constant through the use of a constant pressure gasometer or other device to insure approximately the same rate of vaporization in the still. The latter may be corrected for if necessary by adjusting the depth of immersion of C. This may be facilitated by the use of the scale and pointer arrangement shown in the sketch. The required depth of immersion is first determined by actual operation. The still is partly filled with mercury and started with the device immersed to its full extent. When the mercury level in M reaches the cut-off position, the level of mercury in A is marked and the cut-off device slowly raised until cut-off occurs. The pointer is then fastened rigidly to D so as to coincide with the mark on A. A millimeter scale carrying the notations 720 to 780 mm. to include the normal range of barometric pressures is then mounted on A so that the pointer indicates the barometric pressure at the time of adjustment. Thereafter, in order to have the cut-off occur at the same position in M, it is only necessary to raise or lower the device until the pointer indicates the prevailing atmospheric pressure. A second scale may be attached from which the barometric pressure may be read utilizing the mercury levels in the still-head and filling tube *before* starting the still. This latter method has the added advantage that any slight pressure in the still is automatically compensated for.

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Adaptation of the Diphenylcarbazide Test for Mercury to the Scheme of Qualitative Analysis.—The diphenylcarbazide test for mercury is very delicate, detecting 0.0005 mg. per 2 cc., but its use so far has been restricted to practically neutral solutions.[1]

However, in the confirmation of mercury, both in Group I and in Group II, the solutions are decidedly acid. It has been found that by adding an excess of solid sodium carbonate to such solutions, the presence of considerably less than 0.1 mg. of mercury per cc. can be detected very readily. The procedure outlined below has been used for the past two years with marked success in qualitative analysis courses in this University.

The mercury precipitate in Group I is dissolved in aqua regia, that of Group II is dissolved in hydrochloric acid and sodium chlorate. In either case the solution is evaporated to a volume of about 1 cc., placed in a test-tube and diluted with 5 to 6 cc. of water. Four to eight drops of a saturated alcoholic solution of diphenylcarbazide is added and a large excess of solid sodium carbonate is gradually dropped into the solution. When mercury is present, the foam produced on neutralization assumes a blue tinge, and after the addition of an excess of carbonate the entire solution turns blue.

At the conclusion of the experiment the solution should either be blue or orange to pink in color. If the solution remains colorless, it indicates that the diphenylcarbazide solution has deteriorated.

Freshly prepared diphenylcarbazide solution is colorless, but soon develops a pink to red color. This color does not seem to affect its use for the test. However, on standing for several weeks it finally fails to give a blue color in the presence of mercuric salts. Aqua regia does not interfere provided the test is completed soon after the addition of the diphenylcarbazide solution. If the test solution containing aqua regia is allowed to stand for some hours after the addition of diphenylcarbazide, it will fail to develop any color when an excess of sodium carbonate is added.

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[1] Kolthoff, *Chem. Weekblad*, **21**, 20 (1924); Stock and Pohland, *Z. angew. Chem.*, **39**, 791 (1926).

Neither sodium acetate nor sodium bicarbonate can be successfully substituted for the sodium carbonate in this test.

CONTRIBUTION FROM THE
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF HEMIMELLITIC ACID

BY FRANK C. WHITMORE AND R. P. PERKINS

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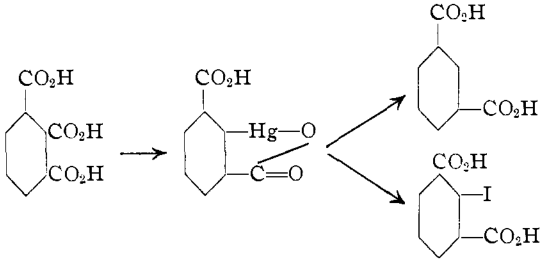
Since the treatment of 3-nitrophthalic acid with mercuric acetate[1] gives over 90% of the calculated amount of the product in which the 2-carboxyl group is replaced by mercury, it seemed desirable to study the effect of other groups on the replacement of one of two ortho carboxyl groups. The simplest case of this kind is presented by hemimellitic acid (benzene-1,2,3-tricarboxylic acid). It was found that the 2-carboxyl is replaced by mercury. No evidence of any replacement of the 1- or 3-carboxyl was found. The structure of the mercury compound was determined by replacing the mercury by hydrogen to give isophthalic acid and by iodine to give 2-iodo-isophthalic acid.



The best method of obtaining the 2-halogen isophthalic acids is undoubtedly by this procedure, starting with hemimellitic acid prepared from acenaphthene.

Experimental

Hemimellitic acid was prepared by a modification of the method of Graebe and Leonhardt.[2] From 100 g. of naphthalic anhydride was obtained 46 g. of hemimellitic acid (44% yield), m. p. 201–203° with decomposition to form the anhydride.

A method is being developed in this Laboratory for the preparation of hemimellitic acid by the direct oxidation of acenaphthene.

A solution of 40 g. (0.2 mole) of hemimellitic anhydride in 110 cc. of 6 *N* sodium

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[1] Whitmore and Culhane, THIS JOURNAL, **51**, 602 (1929).

[2] Graebe and Leonhardt, *Ann.*, **290**, 218 (1896).