# CLIX.—*The Dissociation Constants of Organic Acids. Part III. The Routine Preparation of "Equilibrium" Water and of Moderate Grade Conductivity Water.*

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In connexion with this series of researches, considerable quantities of conductivity water of two grades are required, the first for carrying out the actual conductivity measurements, and the second for the recrystallisation of salts and for other purposes : a slightly higher conductivity is obviously permissible for the latter water. The present paper describes a still whereby both types of water can be *simultaneously* produced, conveniently and in quantity, from ordinary distilled water.

Two types of water may be employed in the accurate study of the conductivity of electrolytes in aqueous solution at high dilutions; "equilibrium" water (Washburn, *J. Amer. Chem. Soc.*, 1918, **40**, 109) with a specific conductivity ($\kappa$) of about 0·8 gemmho at 25°, and "ultra pure conductivity water" with $\kappa < 0{\cdot}1$ gemmho at 25°. The former may be regarded as a saturated solution of carbonic acid under the partial pressure of the carbon dioxide of the atmosphere (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1460, 2460), and by accepting this view the *exact* nature of the "water correction" for solutions of acids, bases, and salts may be determined (*idem, ibid.*, 1917, **39**, 9). Attempts have been made to eliminate or very considerably to reduce the "water correction" in dilute solutions by the use of the higher-grade water, but this necessitates working in closed vessels during the preparation of solutions and measurement of conductivities (compare Kohlrausch, *Z. physikal. Chem.*, 1902, **42**, 200; Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 2461; Hartley and

Barrett, J., 1913, **103**, 789), since on mere exposure to the atmosphere the conductivity rises and ultimately reaches a constant value in contact with pure air of 0·8—0·9 gemmho at 25°. The use of such pure water was therefore ruled out in the present work, as it was considered that its conductivity would change appreciably, and in a manner which could not be accurately determined, under the experimental conditions employed. This fact was early realised by Kohlrausch: all his classical work was carried out with water of $\kappa = 0{\cdot}8$—$1{\cdot}0$ gemmho at 18° (see Kohlrausch and Maltby, *Wiss. Abhandl. Physik.-Techn. Reichsanstalt*, 1900, **3**, 188; Kohlrausch, "Ges. Abh.," 1911, Vol. II, p. 826). We are using slightly better water ($\kappa = 0{\cdot}8$—$0{\cdot}9$ gemmho at 25°), and this possesses the advantage that the nature of the solvent correction, especially for acids, can be determined by making certain plausible assumptions (compare Vogel, J., 1929, 1476, 1487 *).

The stills described in the literature may be divided into two classes: (1) Those producing "ultra pure conductivity water," such as those of Bourdillon (J., 1913, **103**, 791), Wieland (*J. Amer. Chem. Soc.*, 1918, **40**, 131), Kraus and Dexter (*ibid.*, 1922, **44**, 2468), Bencowitz and Hotchkiss (*J. Physical Chem.*, 1925, **29**, 705), Bengough, Stuart, and Lee (J., 1927, 2156), and Stuart and Wormwell (J., 1930, 86); (2) stills for the preparation of "equilibrium" water, as described by Walker and Cormack (J., 1900, **77**, 5), Bousfield (J., 1905, **87**, 740; 1912, **101**, 1443), Hartley, Campbell, and Poole (J., 1908, **93**, 428), and Kendall (*J. Amer. Chem. Soc.*, 1916, **38**, 2463). It is the experience of one of us (A. I. V.) that none of the methods in the second class is trustworthy for the routine preparation of large quantities of "equilibrium" water. The present still has been designed to meet this deficiency.

The working of most conductivity water stills is based on the removal of impurities by a stream of purified air passing through the condensing system during the process of distillation (Bourdillon, Wieland) or by fractional condensation of the steam (Kraus and Dexter). The still now to be described combines both principles, by distilling ordinary distilled water from an alkaline potassium permanganate solution in a current of purified air and simultaneously subjecting it to fractional condensation, and it affords both "equili-

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* For various reasons the specific conductivity of the solvent was subtracted from the total measured conductivity for both the acids and the salts. My present view is that no solvent correction is necessary for the acids when "equilibrium" water is employed (compare Wynne-Jones, *J. Physical Chem.*, 1927, **31**, 1647; Kolthoff, *Rec. trav. chim.*, 1929, **48**, 664), and this error will be rectified in a future communication. The correction will not appreciably affect the magnitudes of the primary dissociation constants, the values of which are regarded as preliminary.—A. I. V.

brium " water * and moderate-grade conductivity water ($\kappa = 1{\cdot}3$ or 1·5 gemmhos at 25° as desired) in quantity in one distillation.

The advantages of the new still are : (1) Its simplicity of construction and operation : in the final form, apart from the conductivity-water containers, it is constructed entirely of metal parts, which may be readily replaced and dismantled, and once it has been set working it requires very little attention. (2) Its relatively low cost. (3) The " equilibrium " water is collected directly in the special flasks in which it is stored, and is therefore little affected by laboratory conditions.

## EXPERIMENTAL.

*Description of Still, Air-purification Train, and Conductivity-water Containers.*†—The copper boiler *A* (Fig. 1), of about 19 litres capacity, is supported in a special metal stand and shield *B*. It is provided with a screw cap and is connected by a pure tin (or heavily tinned copper) tube through two screw unions *D* and *E* to a trap *C*. The siphon arrangement, terminating in the tap *F*, for the waste water is noteworthy; the difference in level between the water in the two arms of the trap is about 8 inches and represents the net reduced pressure under which the still is operated. *C* acts as a trap for the spray, and also for the partial condensation of the steam, about one-sixth of the steam from the boiler being condensed here. The steam then passes up the pure tin tube *G* into the long pure tin tube *H* ; *I* and *J* are two condensers of sheet copper soldered directly to this tube. A 3-litre Pyrex flask *K* is attached to the lower end by means of a well-fitting rubber bung. The upper end of *H* is connected to another condenser *L*, and then by a rubber cork to a 6—7-litre Pyrex flask carrying a siphon tube and air outlet tube as shown. In the original still both the connecting tube *N* and the condenser *L* were of Pyrex glass, the attachment to the long tin tube *H* being made by a tightly fitting rubber cork covered with tin foil. In the final design this was replaced by a pure tin tube, $\frac{1}{2}$ inch in diameter, to which was soldered a copper condenser *L*, connected to *H* by a screw union *O* ; this modification, while in no way affecting the actual working of the still or the quality of the water produced,

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* The conductivity of the " equilibrium " water thus prepared did not change appreciably on exposure to the unadulterated atmosphere of the laboratory, *i.e.*, when the carbon dioxide content was 0·03—0·04%. The soda–lime (" sofnolite ") in the purification train and in the guard tubes was introduced in order to prevent ingress of carbon dioxide when its proportion in the laboratory exceeded this value.

† The still and all accessories, including the conductivity-water containers, may be obtained from Messrs. Baird and Tatlock (London), Ltd., 14–15 Cross St., Hatton Garden, London, E.C. 1.

had the advantage of eliminating all glass parts, and therefore the danger of breakage.

All the soldered joints were made with pure tin.

The air-purification train was attached at $P$ and is shown diagrammatically in Fig. 2. It consists of four wash bottles, each of about 270 c.c. capacity, the first, $B_1$, containing concentrated sulphuric acid to a depth of about 1 inch for the removal of ammonia, and the following three being filled with soda–lime ("sofnolite") for the removal of the carbon dioxide from the incoming air; this stream of purified air controls the fractionation of the steam. It is attached to the still through a bubbler $C_1$ containing conductivity water.

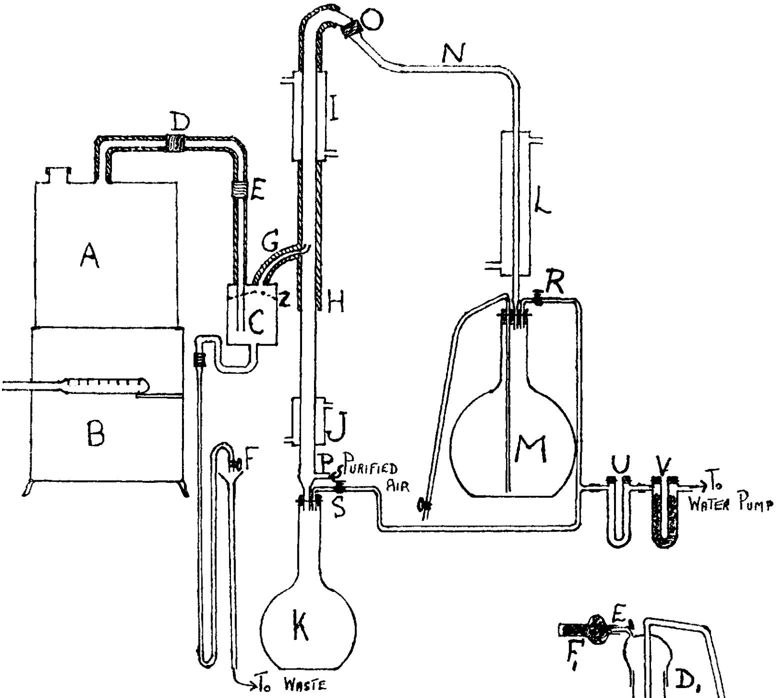

Fig. 1.

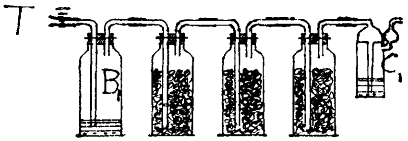

Fig. 2.

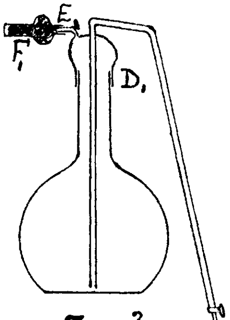

Fig. 3.

The conductivity-water container is shown in Fig. 3. It consists of a 3-litre Pyrex flat-bottomed flask with two ground-glass joints at $D_1$ and $E_1$; $F_1$ is a sofnolite guard tube. The flask fits on to the rubber cork at the lower end of *H*. The water collected in it is exposed only for a very short time to the atmosphere of the laboratory, *viz.*, during the time taken to detach the flask from the still and replace the ground-glass siphon tube at $D_1$. Conductivity water can be kept in these containers for months without appreciable increase in conductivity.

*R*, *S*, and *T* are screw clips for controlling the air supply to the apparatus. The receivers *M* and *K* are connected to a water pump through two **U**-tubes, the first, *U*, being empty and the second, *V*, containing sofnolite or soda–lime.

The shaded portion in Fig. 1 is lagged with cotton wool or other suitable lagging.

On rare occasions a small amount of creeping of the water from the trap *C* into the main condensing column *H* was observed; a perforated plate of pure tin, *Z*, was introduced inside the trap to obviate this.

The condensers *J* and *L* were connected directly to the water supply and always had a rapid stream of water flowing through them. The amount of water flowing through the condenser *I* was controlled by a glass tap in a **T**-piece connected to the water tap, the other arm of which was connected to *J* and *L*.

*Operation of the Still.*—The still as received from the makers contains much grease, etc., and the metal parts must be steamed out for 4—5 days with steam generated from distilled water in the boiler *A*. The conductivity-water containers and siphon tubes must be soaked in chromic acid–sulphuric acid mixture for at least 96 hours, thoroughly washed with distilled water, and then steamed out for at least 24 hours with steam generated from distilled water in an all Pyrex-glass apparatus. After the preliminary steaming the complete still is assembled as in Fig. 1. The boiler is charged with 11—12 litres of distilled water ($\kappa$ = about 3 gemmhos at 25°), together with 30 g. each of potassium permanganate and sodium hydroxide. The burner beneath the boiler is lighted, the tap *F* and the screw clip *S* closed, the screw clip *R* fully and *T* partially opened, and the water pump gently set into operation. During this initial stage owing to the expansion of the air from the boiler, etc., very little air enters at *T*; the water pump is later adjusted so that at most only about one bubble per second passes through the sulphuric acid in $B_1$. When the water is nearly boiling (about 75 minutes) the gas is lowered and the water kept simmering for 30—45 minutes. Screw clip *S* is then opened, *R* closed, and the water allowed to boil gently.

Under these conditions all the steam condenses in *H* and is collected in an ordinary 3-litre Pyrex flask, treated as described above, at *K*. Distillation is carried out at the rate of about 1 litre per hour. As soon as there is steady condensation in *K*, tap *F* is opened and the air supply carefully adjusted at *T*. After 1 hour, *i.e.*, after about 1 litre of water has been collected in *K* (this water may be discarded), screw clip *R* is fully opened and *S* nearly closed. A portion of the steam then passes over into *L*, and the water passing through the condenser *I* is adjusted so that about twice as much steam is condensed in *L* as in *H*; the temperature of the water in the condenser *H* will at steady working be about 80°. After a further hour's running in this manner, the water collecting in *K* has $\kappa = 0{\cdot}8$—$0{\cdot}9$ gemmho at 25°. The receiver *K* is then replaced by the flask of the special container (Fig. 3); tap *F* is closed during the changing of the receivers in order to prevent emptying of the trap. Provided the air supply at *T* has been properly adjusted, distillation into *K* and *M* will continue for another 6—7 hours with little or no attention. After this time, 1—1·5 litres of water remain in the boiler and the conductivity of the water collecting in *K* begins to rise. The distillation is then stopped, tap *F* closed, the conductivity-water container removed and fitted with its ground-glass cap, and an ordinary 3-litre flat-bottomed flask substituted.

The still, when operated in the manner described, delivers in the course of a day's run 1·5—2 litres of equilibrium water with $\kappa = 0{\cdot}8$—0·9 gemmho at 25°, and 4—5 litres of second-grade water with $\kappa =$ 1·2—1·3 gemmhos at 25°.

If the preliminary total condensation in *K* is omitted and the purified air stream arranged so that part of the steam passes over into *L*, the quantity and quality of the "equilibrium" water remain unchanged, but the quantity of the second-grade water is increased to 6—7 litres and its specific conductivity to 1·4—1·5 gemmhos at 25°.

Details of two typical runs are given below. The conductivity was determined by the standard bridge method with a valve oscillator and a telephone detector. A Kohlrausch pattern cell of 35-c.c. capacity was employed, the cell constant being determined by the method of Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 312). All the specific conductivities are expressed in gemmhos at 25°.

| | Run I. | | Run II. | |
|---|---|---|---|---|
| | Volume (litres). | $\kappa$. | Volume (litres). | $\kappa$. |
| First fraction (discarded) | 1·5 | — | 1·6 | — |
| "Equilibrium" water | 1·6 | 0·86 | 1·7 | 0·79 |
| Second-grade water | 4·1 | 1·26 | 4·5 | 1·30 |
| Rejected at trap | 1·7 | — | 1·7 | — |

When the still has been in operation for some weeks, it is unnecessary to measure the specific conductivity of the distillate at various time intervals. The conductivity water in both receivers is collected after definite times from the commencement of the distillation.

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