112. *Separation of the Isotopes of Hydrogen by the Chemical Decomposition of Water, and some Remarks on the Mechanisms underlying the Reducing Action of Dissolving Metals.*

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WHILST engaged in concentrating the new isotope of hydrogen for use as an isotopic indicator in the study of the mechanism of organic reactions, it occurred to us that the material which had resulted from the earlier stages of the electrolytic fractionation of water by Lewis and Macdonald's method (*J. Chem. Physics*, 1933, **1**, 341) could be used for the investigation of a problem connected with the reducing action of dissolving metals.

A metal is regarded as an electron quasi-gas, subject to leakage through the potential wall in its surface. For a system in equilibrium the escaping tendency of the electrons, which must depend *inter alia* on the lattice energy of the metal and the potential function at the interface, is measured by the reversible electrode potential. In reduction, however, the situation is more complicated, partly because the escape of the reducing electron must be aided by the potential field of the molecule undergoing reduction, and partly because the escaping electron is chemically employed in advance of the establishment of any statistical equilibrium. It follows that the energy of the reducing electron originating in any given metal must depend on the substance being reduced, and that the problem of assessing that energy is essentially kinetic in character.

For the case in which the reduced substance is either the oxonium ion or the water molecule, it seemed that some evidence concerning the energies of the reducing electrons of different metals might be obtained from observations of the difference of the speeds with which they attack the two hydrogen isotopes when present in these molecules. From this point of view we may disregard the different molecular species present in any given sample of aqueous acid or of water, and consider the whole system as a reservoir of two reactive bonds, namely the $O\text{–}H^1$ bond and the $O\text{–}H^2$ bond. The known physical properties of heavy water show that in similar states of combination with oxygen the two hydrogen isotopes occupy nearly the same volume and exert nearly the same external electric field. It follows that statistical factors should lead to no considerable discrimination between the isotopes, and that the relative frequencies with which the $O\text{–}H^1$ and $O\text{–}H^2$ bonds are presented for attack should be almost identical with the relative proportions in which they are present. On the other hand, it seems clear from the results of the electrolytic fractionation of water that the energies of rupture of the $O\text{–}H^1$ and $O\text{–}H^2$ bonds differ considerably from each other; and Polanyi has explained how this difference could arise as a consequence of the existence of zero-point energy, and also on account of " tunnelling " by particles of pronounced wave-nature (Cremer and Polanyi, *Z. physikal. Chem.*, 1932, **19**, 443; Polanyi, *Nature*, 1934, **133**, 26). It follows that, although electrons of sufficiently high energy should show no marked discrimination, electrons of lower energy would preferentially attack the more vulnerable linking, and, for any normal kind of energy-distribution between the reducing electrons, a decrease in the average energy should lead to an increase in the selectivity.

The general method of the experiments now recorded was to dissolve the metal or other reagent in a known amount of water, aqueous acid or aqueous alkali, of known diplogen content, and to measure the quantities in which the two isotopes become discharged by burning the evolved hydrogen * and observing the volume and isotopic composition of the water thus formed. In some cases the diplogen content of the residual solution was also determined, but only as a rough check, since isotopic analysis of the discharged gas gives a more accurate measure of the effect under investigation.

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* As Urey, Brickwedde, and Murphy have already urged (*Nature*, 1934, **133**, 173), it seems highly desirable that the ordinary names of elements and compounds (*e.g.*, hydrogen, water, acetylene, and methane) should be taken to include *all* isotopic forms: haplogen and diplogen are both hydrogen; and, logically, the haplon and the diplon are both protons.

Results.—These are summarised in Table I, and the following notes are added in amplification of the tabulated particulars.

TABLE I.

Expt. No.	Re-agent.	Impurities in reagent, wt. %.	Aqueous medium.	Initial vol., c.c.	Initial composition (H^2 atoms %).	Concn., acid or alkali.		Approx. temp.	Combustion water.		α.
						Initial (*N*).	Final (*N*).		Vol., c.c.	Composition (H^2 atoms %).	
Series I. Pure or nearly pure elements.											
1	Li		$H_2O \rightarrow$ aq. LiOH	75	2·42	0·0	9·3	40°	6·3	1·71	1·49
2	,,		$H_2O + H_2SO_4$	91	2·20	8·1	0·4	40	6·3	1·55	1·49
3	Na		$H_2O \rightarrow$ aq. NaOH	125	2·37	0·0	13·9	40	15·6	0·888	2·83
4	,,		$H_2O \rightarrow$ aq. NaOH	100	2·37	0·0	6·5	40	5·9	0·872	2·81
5	,,		$H_2O \rightarrow$ aq. $NaHCO_3$	100	2·37	0·0	17·3	40	15·6	0·850	2·98
6	,,		$H_2O + H_2SO_4$	211	2·28	3·5	0·4	40	5·9	0·801	2·92
7	K		$H_2O \rightarrow$ aq. KOH	100	2·42	0·0	7·0	40	6·3	1·31	1·99
8	,,		$H_2O \rightarrow$ aq. KOH	75	2·42	0·0	8·6	40	5·8	1·32	1·89
9	Mg		$H_2O + H_2SO_4$	121	2·22	7·7	1·8	30	6·5	0·985	2·33
10	,,		$H_2O + H_2SO_4$	121	2·22	7·8	2·2	100	6·1	1·09	2·10
11	Ca		$H_2O \rightarrow$ aq. $Ca(OH)_2$	100	2·37	0·0	saturated	90	4·5	1·55	1·57
12	,,		$H_2O + H_2SO_4$	121	2·18	7·7	1·7	90	6·6	1·69	1·31
13	,,		$H_2O + H_2SO_4$	121	2·18	7·7	0·9	90	7·5	1·72	1·29
14	Zn	Very small trace C	$H_2O + H_2SO_4$	218	2·20	7·8	4·7	90	6·0	0·397	5·6
15	,,		$H_2O + H_2SO_4 +$ equiv. NaCl	100	2·20	7·5	2·0	90	5·1	0·440	5·2
16	Al		$H_2O +$ NaOH	157	2·23	6·4	6·4	90	6·0	0·542	4·25
17	,,		$H_2O + H_2SO_4 +$ trace NaCl	171	2·23	5·4	1·8	90	5·4	0·581	3·95
18	Ce		$H_2O + H_2SO_4 +$ trace NaCl	96	2·16	9·7	6·8	90	2·5	0·897	2·46
19	Si		$H_2O +$ NaOH	79	2·28	6·4	6·4	90	6·0	1·01	2·34
20	Cr		$H_2O + H_2SO_4$	96	2·16	9·7	1·0	90	7·6	0·505	4·49
21	Mn	Traces of Fe, Al and Si	$H_2O + H_2SO_4$	121	2·22	7·7	2·2	90	6·1	0·455	5·1
22	Fe		$H_2O + H_2SO_4$	130	2·15	10·0	6·2	90	4·5	0·513	4·28
23	Co		$H_2O + H_2SO_4$	96	2·16	9·7	2·9	90	5·9	0·549	4·08
Series II. Impure elements.											
24	Zn	Pb, 1·0; C, 0·1%	$H_2O + H_2SO_4$	242	2·18	7·7	4·9	90	6·0	0·327	6·8
25	Al	Zn, 5·8; Cu, 5·8; Si, 0·7%	$H_2O +$ NaOH	157	2·23	6·4	6·4	90	6·0	0·468	4·90
26	,,	,, ,, ,,	$H_2O + H_2SO_4$	171	2·23	5·4	2·1	90	5·0	0·574	4·00
27	Si	Fe, 6·0%; traces Al, Ca and C	$H_2O +$ NaOH	118	2·23	9·2	9·2	90	3·0	1·03	2·22
28	Cr	Fe, 25%; traces Mn, Si and C	$H_2O + H_2SO_4$	96	2·16	10·0	0·1	90	8·6	0·532	4·26
29	Mn	Fe, 2·5; Si, 1·2; Al, 0·5%; trace C	$H_2O + H_2SO_4$	121	2·22	7·7	3·1	40	5·1	0·511	4·27
30	Fe	C, 4·8; Mn, 1·5; Si, 1·0; P, 1·0%	$H_2O + H_2SO_4$	121	2·22	7·7	2·3	90	5·9	0·482	4·73
Series III. Couples.											
31	Zn +	Cu, 3%	$H_2O + H_2SO_4$	196	2·25	4·9	1·5	90	6·0	0·358	6·4
32	,,	Cu, 20%	$H_2O + H_2SO_4$	196	2·25	4·8	1·4	40	6·0	0·320	7·3
33	,,	Cu, 20%	$H_2O + H_2SO_4$	196	2·25	4·8	1·4	90	6·0	0·335	7·0
34	,,	Cu, 50%	$H_2O + H_2SO_4$	196	2·25	4·8	1·4	40	6·0	0·285	8·0
35	,,	Ag, 20%	$H_2O + H_2SO_4$	96	2·16	9·7	3·6	90	5·4	0·407	5·6
36	,,	Au, 3%	$H_2O + H_2SO_4$	117	2·25	6·7	0·0	40	7·0	0·517	4·50
37	,,	Ni, 15%	$H_2O + H_2SO_4$	91	2·20	7·2	0·0	90	5·9	0·384	5·9
Series IV. Amalgams.											
38	Na–Hg	3·0% Na	$H_2O \rightarrow$ aq. NaOH	100	2·42	0·0	3·0	90	2·7	0·768	3·24
39	,,	,, ,,	$H_2O + H_2SO_4$	126	2·18	8·9	3·8	90	6·0	0·640	3·49
Series V. Compounds.											
40	CaH_2	(Note: H_2 equally from CaH_2 and H_2O)	$H_2O \rightarrow$ aq. $Ca(OH)_2$	75	2·42	0·0	saturated	40	8·9	1·12	1·07
41	CaC_2	(Note: C_2H_2 burnt)	$H_2O \rightarrow$ aq. $Ca(OH)_2$	75	2·42	0·0	,,	40	6·0	1·64	1·50
42	Al_4C_3	(Note: CH_4 burnt)	$H_2O + H_2SO_4$	91	2·20	7·2	0·0	90	7·0	1·11	2·03

Col. 2 indicates the reagent. The elements of Series I, all of which are metals except silicon, were employed in the purest forms in which we could obtain them, except zinc (expts. 14 and 15). The difficulty here was that pure zinc is insoluble in dilute sulphuric acid, even in the presence of chloride ions, and we were forced therefore to use a sample which still contained a very small trace of carbon. The pure aluminium and cerium also were insoluble in dilute sulphuric acid, but in these cases the addition of a small amount of sodium chloride brought about dissolution (expts. 17 and 18). The compositions of the impure metals of Series II are shown in col. 3. The silicon–iron and chromium–iron alloys (expts. 27 and 28) were commercial specimens, and the sample of iron (expt. 30) was ordinary cast-iron, about half the carbon which it contained being in the combined form. The couples of Series III were prepared from pure zinc. Copper (expts. 31—34) was deposited by the addition of anhydrous copper sulphate to the dilute sulphuric acid employed to dissolve the zinc, the addition being repeated from time to time during the progress of the dissolution. The total amount of copper thus added is expressed in the table as parts by weight per cent. parts of zinc. The copper tended to become detached from the zinc during solution, so that, despite the distributed addition of the copper, the couple tended to lose its efficacy; only in the case in which 50% of copper was added, when the solution remained blue throughout the whole time of the reaction, can it be assumed that the zinc was always effectively coupled (expt. 34). The other metallic couples (expts. 35—37) were more coherent; silver was deposited from silver sulphate, gold from sodium aurichloride, and nickel from nickel oxide. The amalgams of Series IV (expts. 38 and 39) were prepared from distilled mercury. The hydride and carbides of Series V (expts. 40—42) were commercial specimens.

The solvent media employed are indicated in col. 4. Thus, in expt. 1, lithium was added to water, so that the medium, originally neutral, was alkaline throughout the process of solution; in expt. 2, the metal was added to dilute sulphuric acid present in excess; and in expt. 5, sodium was added to water, whilst an excess of carbon dioxide was passed through the solution during the period of the reaction. For the heavy metals, the solvent most frequently employed was dilute sulphuric acid, but, as indicated above, it was necessary to introduce a small amount of sodium chloride in order to secure solution of the pure aluminium and cerium (expts. 17 and 18); and the effect of the addition of a large amount of sodium chloride was examined in the case of zinc (expt. 15). Aqueous sodium hydroxide was also employed in certain instances, notably for the solution of aluminium and silicon (expts. 16, 19, 25 and 27).

Cols. 5 and 6 record respectively the initial volume of the aqueous solution and its initial isotopic composition, the latter value being expressed in atoms of diplogen per cent. atoms of hydrogen (*i.e.*, haplogen plus diplogen). The water employed for these experiments contained 2·37 or 2·42 atoms % of diplogen, but as any initially added sulphuric acid or sodium hydroxide contained much haplogen but very little diplogen, the initial diplogen content of the various aqueous solutions employed was somewhat smaller than that of the water used in their preparation. Cols. 7 and 8 indicate the initial and the final values of the acidity or alkalinity of the medium, any change of volume being neglected in the calculation of the final value. The reaction of the medium was never allowed to change from acid to alkaline during a single experiment, and the initial and the final figures for any one experiment therefore refer always to the same reaction, acidity or alkalinity, as the case may be. It was not found possible accurately to control the temperature, and the values recorded in col. 9 are therefore only approximate.

Cols. 10 and 11 contain respectively the volume and the isotopic composition of the samples of water which were obtained by burning the evolved hydrogen, or, in expts. 41 and 42, the acetylene or the methane (see footnote, p. 493). In col. 11 the second place of decimals is accurate, but the third, where a third is recorded, is subject to an error of several units. All isotopic compositions were obtained by comparison of the densities of the water samples with the density of ordinary water, the error of the measurement being about $\pm$ 2 parts per million. For the calculation of the composition from these relative densities, it is necessary to know the diplogen content of ordinary water, and for this purpose we have adopted Lewis and Macdonald's value 0·015% (*loc. cit.*), as we have not yet made an accurate isotopic analysis of London water.

The last column of the table contains the calculated values of the isotopic separation coefficient α. This is defined in the manner analogous to that used by Lewis and Macdonald (*loc. cit.*) in connexion with the electrolytic fractionation of water. If n_1 and n_2 are the number of atoms of haplogen and diplogen respectively which are present in the solution at any moment during the reaction in which hydrogen is being discharged, then, for an infinitesimal discharge, $(dn_1/n_1) = \alpha(dn_2/n_2)$, so that, for a finite discharge of hydrogen, $\log(n_1'/n_1'') = \alpha \log(n_2'/n_2'')$. As the proportion of water decomposed was usually small (of the order of 5% in most of the expts.), the question whether α would in all cases remain constant throughout a completed decomposition of water scarcely arises: the coefficient could in any event be regarded as a ratio of initial specific velocities.

DISCUSSION.

A selection of the above results, including those relating to sodium, has already been recorded (*Nature*, 1934, **133**, 291). Two notes, one by Davis and Johnston (*J. Amer.*

Chem. Soc., 1934, **56**, 492) and the other by Horiuti and Szabo (*Nature*, 1934, **133**, 227), each reporting experiments on the decomposition of water by sodium, appeared too late to permit reference in our preliminary publication. The results of these experiments are in accord with ours. Davis and Johnston give α as 2·5, but the concentrations of diplogen employed by them were so low that the calculated result is sensitive to the assumed value for the diplogen content of ordinary water; within the limits of this uncertainty their value is identical with our 2·8. They, like ourselves, decomposed only a small proportion of the water, but Horiuti and Szabo converted their water completely into sodium hydroxide and hydrogen, and their results therefore constitute a strong indication that the separation coefficient, α, remains nearly constant during the progress of decomposition.

A comparison of the results of duplicate experiments such as nos. 3 and 4, 7 and 8, and 12 and 13, shows that the values obtained for the separation coefficient are closely reproducible. Expts. 9 and 10 indicate that, within the range of the observation, the effect of temperature on the separation coefficient is small in comparison with the effects which remain to be considered. It is, of course, consistent that the experiment at the lower temperature should yield a slightly higher degree of separation; it appears, nevertheless, that the coefficients, α, may be regarded as nearly constant characteristics of the reagents and the media.

Reference to the results of the experiments of Series II, III and IV shows that the presence of impurities in the reagent has a large effect on the separation coefficient. This is to be expected, since the impurities will form with the principal metal either alloys or couples or both, and in any event the hydrogen is likely to be liberated to a large extent at the surface of the impurities. The main exception is silicon (expts. 19 and 27); but this is an electrical non-conductor, and its dissolution proceeds, no doubt, without marked electrical interchange between the element itself and its impurities.

The results of the expts. of Series I may now be considered in further detail. If we start from the view that decompositions are essentially electrochemical, selectivity depending on the energy of the escaping electron as suggested at the outset, there are two electrical potential series with which we might endeavour to connect the separation coefficients, in spite of the irreversible character of the processes to which the latter refer. In the first row of Table II the metals are arranged in the order of their single electrode potentials; in the second row, they are placed in order of their photo-electric potentials; the two series agree. The lower lines of the table contain the separation coefficients which are adopted on the basis of the experiments of Series I; the reason for the distribution of these values in three rows is indicated later.

TABLE II.

Single electrode potentials	K	Na	—	Ca	Mg	Al	Mn	Zn	Cr	Fe	Co	—
Photo-electric potentials	K	Na	Li	Ca	—	Al	—	Zn	—	Fe	—	—
(A) $\alpha[H_3O^{\oplus}]$	—	—	—	1·3	2·1	4·0	5·1	5·6	4·5	4·3	4·1	—
(B) $\alpha[H_2O]$	1·9	2·8	1·5	—	—	—	—	—	—	—	—	Si
(C) $\alpha[HO^{\ominus}]$	—	—	—	—	—	4·3	—	—	—	—	—	2·3

First, considering the data as a whole, it is seen that the coefficients follow the trend of the two potential series in the middle section of the table, that is, from calcium to zinc inclusive; but to the left of calcium, and to the right of zinc, the correspondence fails. In the region of agreement the variation of the figures is in the expected direction, the metal from which electrons escape most readily showing the smallest discrimination between haplogen and diplogen. The first of the two anomalies relates to the alkali metals potassium, sodium and lithium, for which the separation coefficients are higher than might have been expected, and are notably irregular; the second anomaly concerns the transition metals chromium, iron and cobalt, the separation coefficients for which, instead of continuing to increase above the value for zinc, progressively diminish.

The most probable explanation of the anomaly of the alkali metals would appear to be that suggested to us by Professor Polanyi, namely, that reduction by these metals does not proceed by the electrochemical mechanism already indicated, but depends on the attachment of water molecules *through their oxygen atoms* to the metallic surface, and the subsequent elimination of hydrogen from two bound molecules, in accordance with the mechanism advanced by Horiuti and Szabo (*loc. cit.*). This idea receives support from a number of sources, for instance, from the special position of the alkali metals in reference to the formation of ketyls, the production of which evidently depends on the affinity of the metal for combined oxygen. Our results contain a further indication in the same direction; for, whereas other metals, such as calcium and aluminium, which decompose both acid and alkaline aqueous solutions, give different separation coefficients in the two cases, the coefficients relating to the alkali metals are substantially independent of the reaction of the medium. The conclusions which we would draw are as follows. In an example such as zinc, which is soluble only in acid solution, reduction can scarcely be regarded otherwise than as electrochemical: it results from the attack of the electron on the positive ion. For metals such as calcium and aluminium, which are soluble both in acid and in alkaline media with different separation coefficients, the difference may be taken to indicate that the hydrogen ion when present in quantity is the entity attacked, although when it is absent the reaction proceeds either with water or with hydroxide ions. Correspondingly, the identity of the separation coefficients exhibited by sodium and by lithium in reactions with acidic and alkaline solutions strongly suggests that, whether hydrogen ions are present or not, the entity decomposed is always the water molecule. This would be scarcely comprehensible, were the attack initiated by the metallic electron; for an electron which demonstrably could distinguish between a haplogen bond and a diplogen bond would be expected overwhelmingly to prefer an oxonium ion to a water molecule.

A simple extension of the same argument shows that the reactions of aluminium and of silicon with alkalis are probably initiated by the attack, not of water molecules, but of hydroxide ions, which likewise become bound through their oxygen atoms to the surface of the element, and by thus filling up its valency electron-shell determine the eventual liberation of aluminate or silicate ions.

The reasons underlying the classification of separation coefficients, which is adopted in the construction of Table II, will now be clear: each of the series designated (A), (B) and (C) corresponds to a different mechanism. The first represents electron–proton interaction, and the second and third two different forms of surface-oxidation. Only the separation coefficients of series (A) are regarded as essentially of electrochemical significance, and as subject to a minimum of disturbance from more specifically chemical affinities.

The explanation which we suggest for the anomaly of the transition metals is that the liberation of hydrogen at the surface of these elements is complicated by catalysis of the hydrogen–water exchange. Chromium, iron and cobalt are known to be catalysts for hydrogenation processes, and we imagine that, if the transition series could have been extended to palladium and platinum, the separation coefficients would have further decreased to values more closely approximating to that which corresponds to an equilibrium in the partition of diplogen between molecular hydrogen and water.

A similar anomaly is apparent in the separation coefficients of the zinc–metal couples of series III. The order of increasing electrode potential differences is Ni, Cu, Ag, Au, and the corresponding separation coefficients are respectively 5·9, 8·0, 5·6, 4·5. For the last three members of this series, the separation coefficients regularly decrease, but nickel might have been expected to give a higher value than copper, and the circumstance that it does not may once again be attributed to catalysis of the hydrogen–water exchange.

The separation coefficients for sodium amalgam (series IV) seem to indicate that this material acts partly electrochemically as a molecular sodium–mercury couple, and partly by the surface-oxidation mechanism of sodium itself. The former process should be favoured by acidification of the medium and by dilution of the amalgam, and the manner in which the separation coefficients should change with these conditions can easily be deduced.

With regard to the experiments of series V, it is possibly questionable whether the hydrogen of the calcium hydride (expt. 40) is directly liberated, or whether it is first passed in the form of protons (see footnote, p. 493) to the oxygen atoms of the water. Having regard to the known ionic constitution of lithium hydride, we have taken the view that the hydrogen separates from the calcium in the form of hydride anions, which then decompose the water electrochemically; and, as is indicated by the note in col. 3 of Table I, we have calculated the separation coefficient on that assumption. The result seems to correspond to the great instability which would be expected to characterise the binding of the electrons in the hydride anion. Concerning the experiments of the generation of hydrocarbons, it may be noted that, since acetylene is ionisable in certain circumstances, there is some probability that the separation coefficient relating to the formation of this substance may have been affected by the incursion of an acetylene–water exchange.

Finally, we may again refer to the three hypothetical mechanisms (A), (B) and (C) in order to suggest that, although our experiments have direct reference only to the reduction of water, these mechanisms are typical of possible mechanisms for the reduction by metals of oxygen and halogen compounds generally. For example, no *one* mechanism can be thought to cover two such different processes as the reduction of a ketone by Clemmensen's method and its reduction to a pinacol by the direct action of magnesium-amalgam or sodium : evidently the first process is determined by electronic attack, and the second by a metal–oxygen union.

EXPERIMENTAL.

The reagents were added as gradually as was necessary to the measured volume of water, aqueous acid, or aqueous alkali, through a tube which dipped under the surface of the liquid, the atmosphere initially present being air, or, in the case of easily oxidisable reagents, nitrogen. The reactions of the alkali metals were further moderated by the addition of a layer of high-boiling ligroin, which caused these metals to float mainly in the hydrocarbon and to dip only slightly into the aqueous layer. The evolved hydrogen, after passage through an efficient reflux condenser and a tube cooled in liquid air, was usually directly burnt on red-hot copper oxide, although in expts. nos. 3 and 5 it was first collected in an aspirator over paraffin, and subsequently burnt with a small excess of oxygen from a cylinder; in this process the gases were introduced through separate nozzles into a copper Liebig's condenser, containing a white-hot platinum filament. In expts. 41 and 42, in which the evolved gas was not hydrogen but acetylene or methane, the liquid-air bath was replaced by a bath of solid carbon dioxide and acetone, the combustion being carried out on copper oxide exactly as in the case of hydrogen.

The samples of water obtained by combustion were carefully distilled and out-gassed, and their densities were measured pyknometrically in collaboration with Mr. J. N. E. Day. The pyknometers, which were of 1 to 3 c.c. capacity, were made in pairs, identical in form and size, and from the same sample of glass, one of each pair being filled with water and sealed at both ends for use as a counterpoise. They were of the ordinary U-form with two very fine-drawn capillary tubes, one having a tip and the other bearing a scratch. No caps were used, as the loss in weight, due to evaporation from the capillary tubes during the period required for the measurement, was too small to be detected on a microbalance, provided that, immediately after setting, the water meniscus was drawn back from the tip into the lower part of the corresponding capillary tube. After setting at 25° in a thermostat, the temperature of which remained constant throughout the whole period of the measurements to well within 0·01°, the pyknometer was at once transferred to a bath of water at room temperature, and a rubber pad was pressed against the end of the capillary tube with the scratch in order to cause recession of the meniscus in the other capillary tube during cooling. The final preparations for weighing were carried out with the precautions usual in micro-analytical work, the counterpoise, after immersion in the same baths as the pyknometer, being treated in an identical way. All densities were determined relatively to that of permanganate-treated, distilled, and out-gassed London water.

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