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The Ageing of Standard Cells: Increased Accuracy in their Use: And International Comparisons

A. Norman Shaw, H. E. Reilley and R. J. Clark

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IV. *The Ageing of Standard Cells: Increased Accuracy in their Use: and International Comparisons.*

By A. Norman Shaw, *F.R.S.C.*, H. E. Reilley *and* R. J. Clark, *McGill University, Montreal.*

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Contents.

Section 1.—Introduction and Summary.

The results of this investigation have arisen as a further outcome of the long series of McGill researches on standard cells, originally started by H. L. Callendar, F.R.S., in 1896, and continued for several years by H. T. Barnes, F.R.S.; they may be regarded as a new by-product of the investigation on the absolute measurement of the electromotive force of the normal Weston Standard Cell, conducted by A. N. Shaw from 1909–1911, and described in the 'Philosophical Transactions' in 1913 (*loc. cit.*). It is, however,

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considered that the present contribution brings forward entirely new points of considerable importance, and it is in no sense whatever a recapitulation or further treatment of results discussed in earlier articles. Apart from the descriptive data about apparatus and old cells, contained in former papers,* the results recorded now, and the treatment developed, constitute an independent investigation.

The division of work between the three authors has been as follows :—

R. J. Clark constructed over fifty cells in 1923, performing independently the whole of the detailed chemical and physical procedures involved in the preparation of the ingredients and in the completion of cells of high grade. The construction of these new cells in 1923 was an essential feature of this investigation, without which we would have failed to discover these new methods.

H. E. Reilley, in addition to reconditioning and improving the thermostat and electrical equipment, has performed all the experimental work associated with the observation of cell voltages here, since 1919.

A. N. Shaw carried on the investigation in connection with other studies on cells, from 1908 to 1919, and since 1919 has guided the investigation, contributing the theoretical and numerical work associated with the analysis of the observations, the evaluation of ageing, and its applications; he has also written this communication.

In regard to the establishment of our present cell laboratory in 1908, it is a pleasure to record again our indebtedness to Dr. H. T. Barnes, F.R.S., Dr. H. L. Bronson, and Mr. R. O. King. In particular do we extend our thanks also to the authorities at the National Physical Laboratory in England, and at the Bureau of Standards in the United States, for their continued interest and advice in connection with numerous exchanges of cells. We are gratefully indebted to the Eppley Institute for the donation of a valuable potentiometer.

Much useful advice has been received from Dr. O. Maass on the Physical Chemistry of the cell, and for many years we have been indebted to Dr. A. S. Eve, the Director of the Macdonald Physical Laboratory at McGill University, for his kind encouragement of this investigation. We are also grateful to Mr. H. W. Harkness for assistance in draughting.

Throughout the paper the liberty is taken of using the words *life*, *ageing*, *younger*, *older*, etc., in application to Standard Weston Cells; we feel that no apology for this personification is necessary, in view of their obvious convenience in shortening the phraseology; there can surely be no risk of ambiguity or confusion with the living cells of biology.

* Callendar and Barnes, 'Roy. Soc. Proc.,' vol 62, p. 117 (1897).
Barnes, 'Phil. Trans.,' A, vol. 199, p. 159 (1902).
Bronson and Shaw, 'Brit. Ass. Rep.,' vol. 79, p. 396 (1909).
Bronson and Shaw, 'The Electrician,' vol. 66, p. 698 (1911).
Shaw, 'Phil. Trans.,' A, vol. 214, pp. 147–198 (1913).
Shaw and Reilley, 'Trans. Roy. Soc. Can.,' vol. 13, pp. 171–176 (1919).

The following is a short summary of the main contributions in this article :—

Summary.

1. Neutral Weston Standard Cells are shown to age for at least twenty years according to the equation

$$E_M = A + B \log (M + \tau)$$

where E_M is the change in voltage for an age of M months, and A, B and τ are constants.

2. It is found that an initial reference mean for voltage can be recaptured from time to time as required, to within one or two parts in a million, without the construction of new cells. This constitutes an advance in precision.

3. A theory for the ageing is developed, leading to the more general formulæ

$$E = E_0 + B \log \frac{1 - e^{-k(t+\tau)}}{1 - e^{-k\tau}} = E_F + B \log (1 - e^{-k(t+\tau)}),$$

of which the formula above is an approximation, when k is small. (E_0 = total e.m.f. when $t = 0$, and E_F = total e.m.f. when $t = \infty$, if other effects are ignored.)

4. Detailed instructions for the determination of E_0, B, τ, k and E_F are given. If t is in months it is shown that $B = -17{\cdot}1$ for all neutral cells investigated, and that τ ranges from about $0{\cdot}5$ to 5 months in most cells, with occasional values as high as 25. The possible physical meaning of these constants is discussed in detail and a consistent interpretation of the phenomenon is obtained.

5. Tables and curves for records involving many hundred readings taken over a period of twenty years are submitted to indicate the procedure, and to verify the accuracy.

6. A table and chart of international comparisons of the revised McGill readings with those of the National Physical Laboratory, Teddington, England, and the Bureau of Standards, Washington, show an average difference of zero from Washington for eight exchanges, with a maximum divergence of 6 microvolts, while for five exchanges with Teddington the average difference was 1 microvolt, with a maximum of 8. It is claimed that these differences are due to the disturbances of the transported cells, and to the fluctuations in the reference means. If properly selected batches, corrected for ageing, are used, it is considered that a definite international reference mean could be recaptured when required, to within one part in a million.

Section 2.—The Experimental Determination of the Ageing.

If the rate of ageing of a reference batch of cells is unknown the first essential is to recapture a given initial reference mean, in terms of which each cell reading may be expressed. In the sections on the determination of the important constant B, and on the international comparisons, explanatory references are made to this procedure, and in addition, because of its wider applications, a separate account with instructions as to

detail, is given in Appendices A and B. Having expressed our various readings for all dates in terms of the initially chosen reference mean, a considerable amount of analysis is still required in order to determine whether the character of the ageing is erratic, or whether it may be evaluated systematically for properly chosen batches of sufficient size to permit the elimination of minor variations.

The methods of observation, and the details in regard to many of the cells, are recorded in the papers by BRONSON, SHAW and REILLEY (*loc. cit.*), and attention is also called to the remarks at the end of Section 5.

The records of a series of batches were analysed, but it will be adequate to present the results for the two cases which involve the largest amount of evidence. Other batches were amenable to the same analysis, and gave similar results.

In Table I we show results covering ten years for thirty cells, and twenty years for seven cells. Each figure is the mean for all the cells indicated, and in each case the mean of several readings for each cell is also involved. Approximately 1,800 separate cell comparisons are involved in the compilation of this table, and in each case the readings have been re-expressed in terms of the initial reference mean which had been recaptured for each date by at least two independent methods. The absence of observations for long periods was not found to be a serious loss, as will be seen by the satisfactory continuity shown in figs. 1 and 2. It will be noted that Cells VI and N are named twice; this is done because their behaviour was exceptionally free from temporary disturbances, and because we had so few cells of the required grade, with records extending over the whole twenty years.

TABLE I (see figs. 1 and 2).—Ageing of Neutral Standard Weston Cells.

(Each reading gives the difference from the initial reference mean, in millionths of a volt.)

Age of each cell in months	1	3	6	10	18	24	30	40	50	120	170	180	190	230	240
Mean readings for Cells IV, VI, (VI) A, B, C 5, N, (N) and Q 3	+27	+14	+8	−3	−12	−17	−19	−25	−29	−46	−50	−52	−53	−53	−57

Age of each cell in months	1	2	3	6	8	10	12	15	20	25	30	35	40	50	60	120
Mean readings for thirty neutral cells*	+20	+12	+6	−3	−7	−11	−14	−19	−23	−26	−29	−32	−34	−38	−41	−53

* The thirty cells are P 1, P 2, P 3, P 4, P 5, Q 2, Q 3, Q 4, Q 5, Q 6, IV, VI, VIII, A, B, C 2, C 3, D, N, O, 60, 63, 64, 66, 67, 68, 69, 71, 78 and 79.

TABLE II (see figs. 1 and 2).—Ageing of Acid Standard Weston Cells.

(Each reading gives the difference from the initial reference mean for neutral cells, in millionths of a volt.)

Age of each cell in months	1	3	6·5	8	20	24	47	48	58	59	65
Mean readings for Cells 53, 56, 57, 59, 80*n*, 82, 83	—66	—66	—65	—66	—67	—69	—67	—70	—69	—69	—69

In order to compare these results with those for acid cells, Table II is submitted; in this case approximately 250 readings are involved. Reference is made in the section on the constant B, to their use in connection with its determination, and again in Section 5.

The results of Tables I and II are shown graphically in fig. 1. The circles and squares represent the means for the actual observations, and the curves are given by the formulæ stated in the caption. These formulæ are derived and interpreted below, but we may note that whatever value attaches to the theoretical discussion they

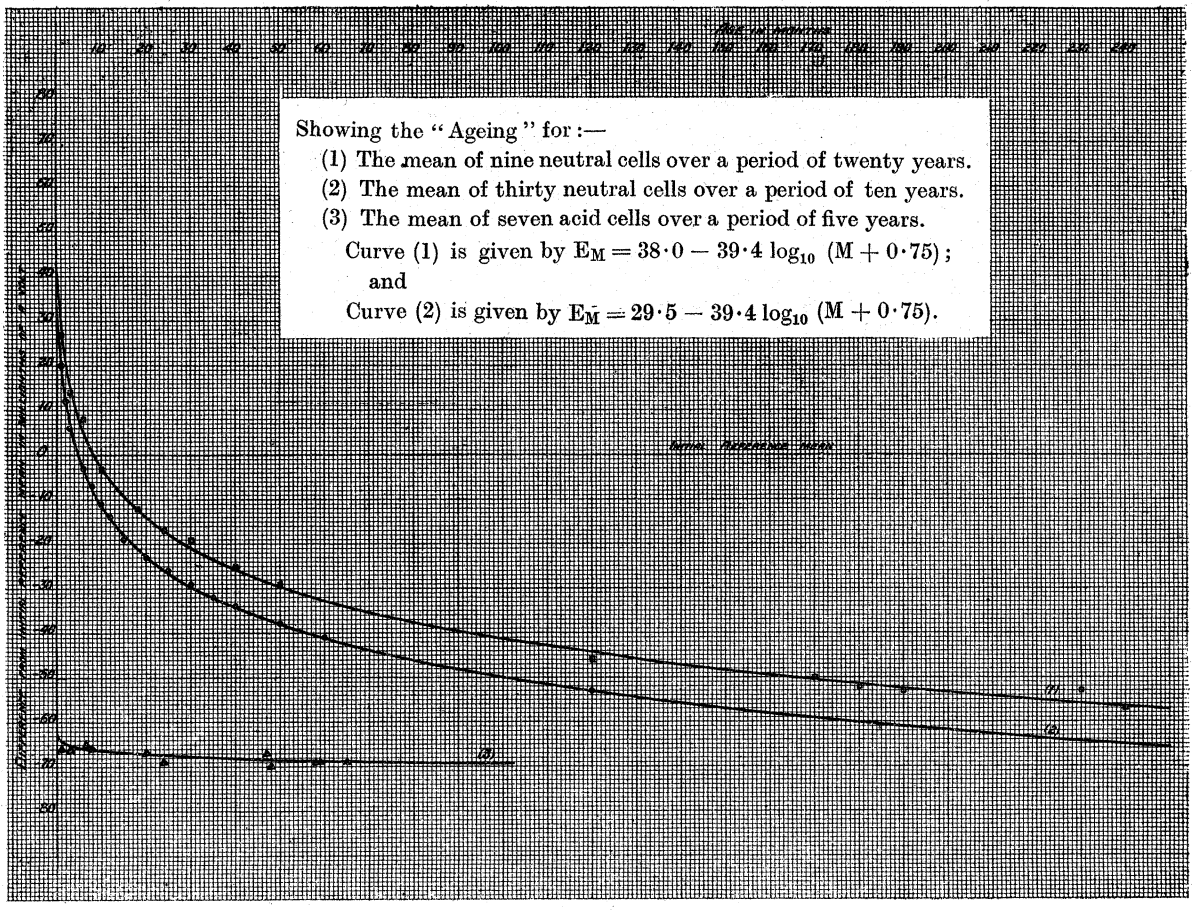

FIG. 1.

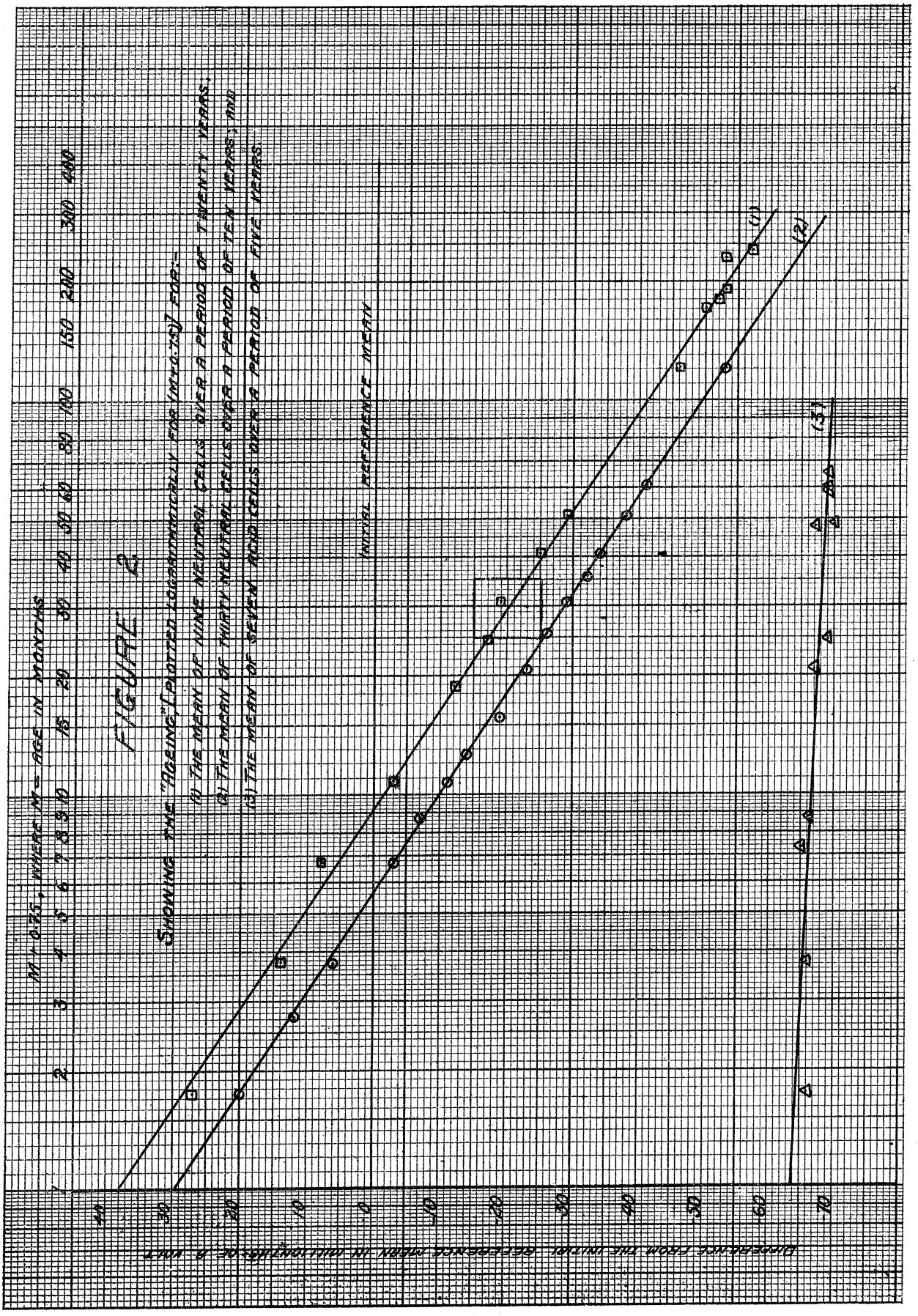

FIG. 2.

undoubtedly hold, at least empirically, as a representation of the observed ageing, to an accuracy that is, as far as we know, of unparalleled precision in this field of work.

By plotting on semi-logarithmic paper, as in fig. 2, the validity of the formulæ becomes strikingly apparent, and the use of it as a means of prediction at once obvious.

In every case for all batches lines were found to be parallel to those in fig. 2. In the formula

$$E_M = A + B \log (M + \tau),$$

this means that the constant B is the same for all cells. It will be observed that we must plot $M + \tau$, not M. The constant A may vary from batch to batch and so may the constant τ. The slope in fig. 2 is not affected by the magnitude of A; but if τ were ignored, the lines would curve downward from their position at the top on the left in fig. 2; this indicates that cells of slow preliminary ageing must have high values of τ in their ageing formula. In view of the detailed discussion below it is unnecessary to develop these points further here. It is sufficient to add that plotting in this manner gives a systematic and consistent evaluation of the ageing in a manner which is both new and precise.

In fig. 3 a number of ideal cases are given, as calculated from typical formulæ. All

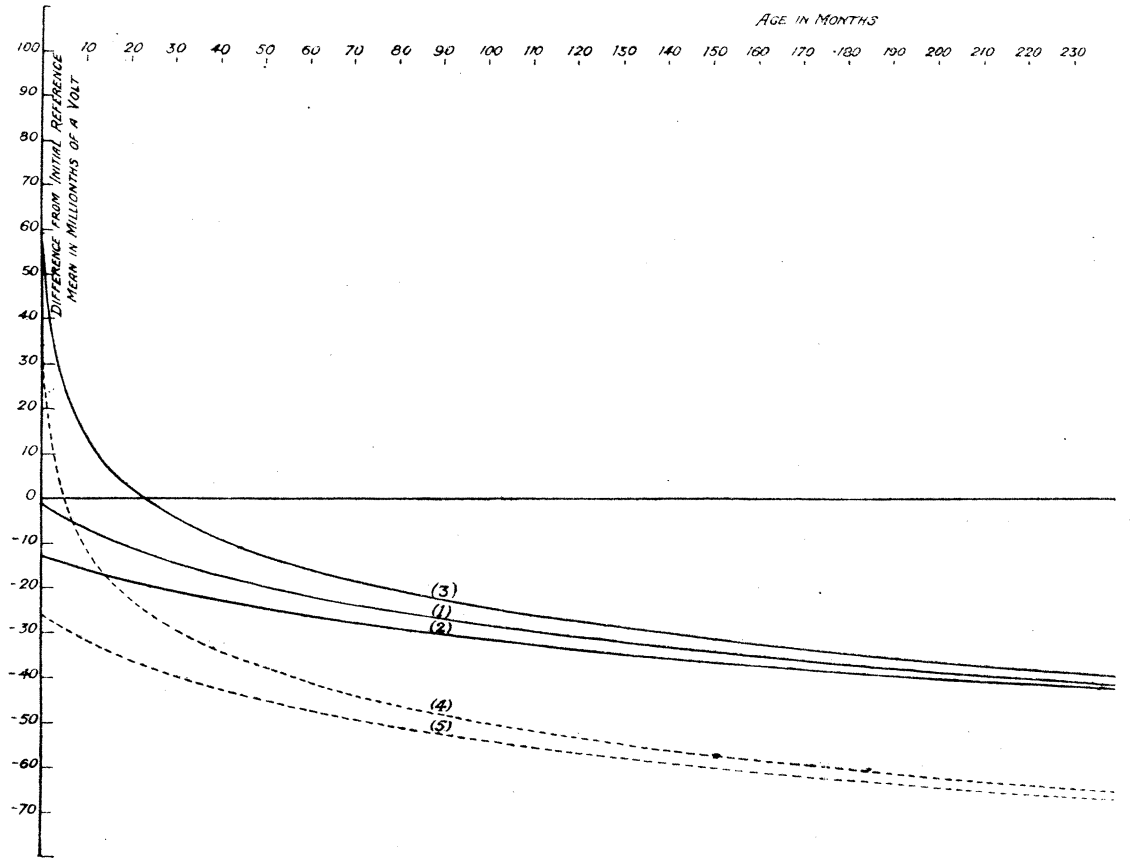

FIG. 3.—Ageing of Individual Cells.—Sample Types. (1) $E_M = 54{\cdot}5 - 39{\cdot}4 \log_{10} (M + 25)$.
(2) $E = 54{\cdot}5 - 39{\cdot}4 \log_{10} (M + 50)$.
(3) $E_M = 54{\cdot}5 - 39{\cdot}4 \log_{10} (M + 0{\cdot}75)$.
(4) $E_M = 29{\cdot}5 - 39{\cdot}4 \log_{10} (M + 0{\cdot}75)$.
(5) $E_M = 29{\cdot}5 - 39{\cdot}4 \log_{10} (M + 25)$.

the cells we examined fell within the zone covered by these curves, and the majority were in close proximity to curve No. 4, which is the same as curve 2 in fig. 1.

In fig. 4 the rates of ageing for various types of cells have been calculated on the basis of our equations (see Section 3 (*b*) below). The majority of our cells lay between the one for $\tau = 5$, and $\tau = 0{\cdot}5$, the latter of which is not shown, but its position is apparent, as the theoretical limit for $\tau = 0$ is shown. It would appear that the majority of the

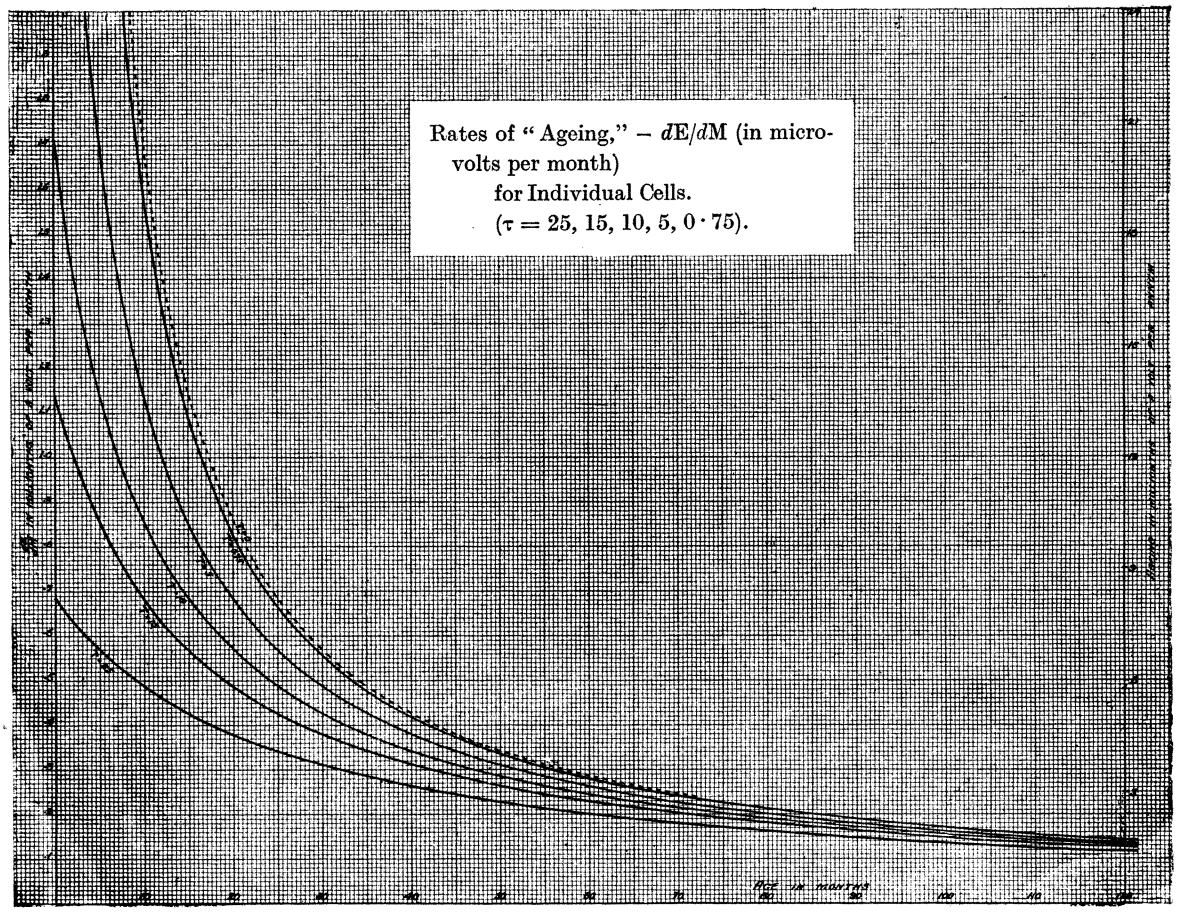

FIG. 4.

early reference cells at the Bureau of Standards would give curves nearer to that for $\tau = 25$.

Table III submits more useful information of the same kind, and shows clearly the important influence of τ on the ageing of young cells, if τ is small; and on the other hand its relative unimportance in the case of old neutral cells of all kinds.

It is of interest to note what errors may arise if the formulæ are applied to individual cells. Fig. 5 illustrates this point clearly for a typical good and a typical bad case of agreement. Even in the case of individual cells the formula remains of some use, when we consider that the plotting is in millionths of a volt.

TABLE III.—Rates of Ageing, in microvolts per month, at Various Ages, for Neutral Cells with Typical Values of τ.

τ	Cells 0 months old.	Cells 3 months old.	Cells 6 months old.	Cells 1 year old.	Cells 2 years old.	Cells 5 years old.	Cells 10 years old.	Cells 20 years old.
0·5	34·2	4·9	2·6	1·4	0·70	0·28	0·14	0·07
0·75	22·8	4·6	2·5	1·3	0·69	0·28	0·14	0·07
1·0	17·1	4·3	2·4	1·3	0·68	0·28	0·14	0·07
5·0	3·4	2·1	1·6	1·0	0·59	0·26	0·14	0·07
10·0	1·7	1·3	1·1	0·78	0·50	0·24	0·13	0·07
15·0	1·1	0·95	0·81	0·63	0·44	0·23	0·13	0·07
20·0	0·85	0·74	0·66	0·53	0·39	0·21	0·12	0·07
25·0	0·68	0·61	0·55	0·46	0·35	0·20	0·12	0·06

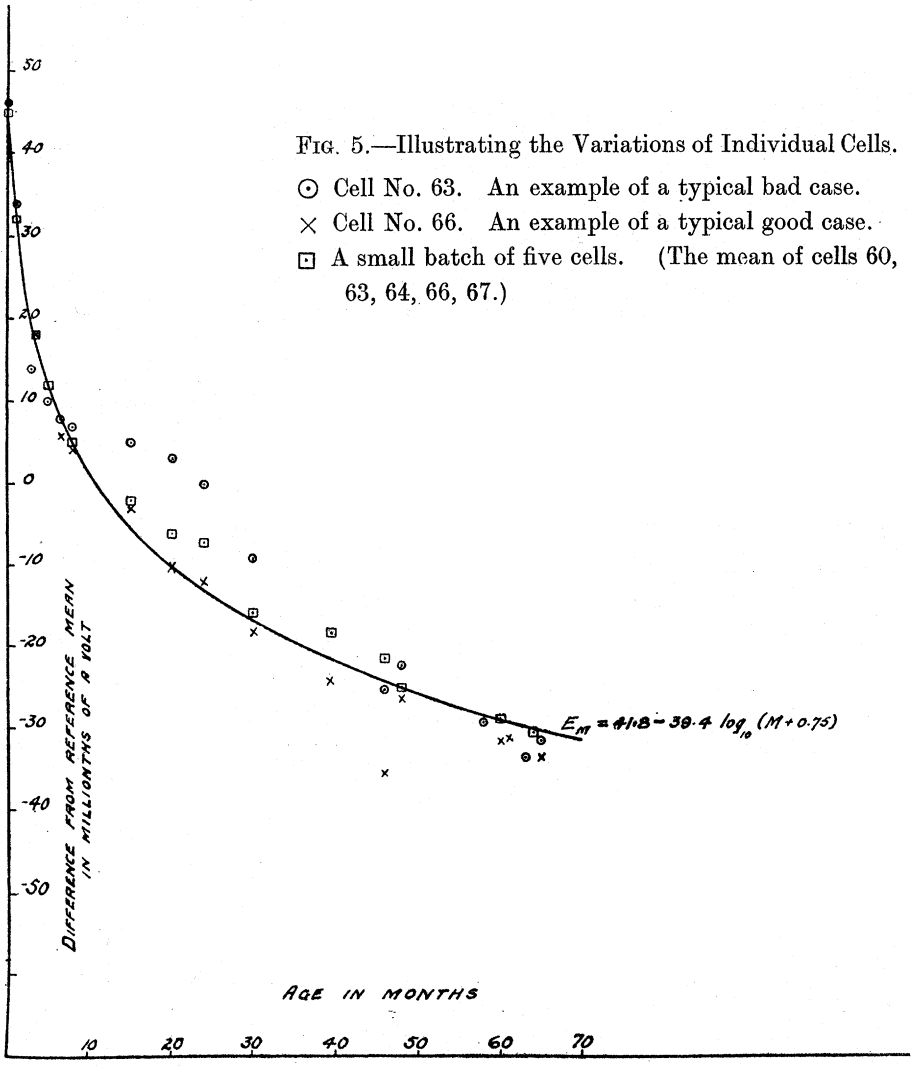

FIG. 5.—Illustrating the Variations of Individual Cells.

⊙ Cell No. 63. An example of a typical bad case.

× Cell No. 66. An example of a typical good case.

⊡ A small batch of five cells. (The mean of cells 60, 63, 64, 66, 67.)

It is of course understood, throughout, that only cells that have been free from disturbing influences are included in these records. The typical bad case mentioned above is not the kind that arises from mal-treatment, but only an extreme example observed when we confine ourselves to the carefully selected cells of uniform behaviour at each period of observation.

The procedure for the accurate evaluation of the constants in the " ageing " formulæ is given in detail in Section 4.

Section 3.—Theoretical Treatment.

(*a*) *Qualitative Discussion of the Phenomenon.*

It is of interest to review some of the factors which have been suggested as possibly responsible for ageing in normal neutral Weston cells.

(1) *The change in particle size of the crystals.*—This effect should not persist over a long period of years in a uniform manner, particularly as the cells have frequently varied from 25° C. to room temperature. If appreciable a change in e.m.f. due to this factor would be undetectable after a few days.

(2) *Change in concentration of the amalgam.*—At the concentrations used a sufficiently large amount of cadmium could not be transported to or from the amalgam limb, to account for the changes observed; nor would any change due to this factor fall off in the logarithmic manner observed in the main effect.

(3) *Slow solution of platinum from the electrodes at different rates in the two cell limbs.*—Slow amalgamation of the platinum has been found to take place, but no difference between the two limbs was detectable in the visual inspection of old electrode wires; it is, however, probable that a slight difference may occur. If the change in voltage due to any possible differences in these rates of platinum amalgamation, or rather, of the appearance of platinum in the mercury and in the amalgam, varied in a logarithmic manner the analysis below would be applicable with minor corrections. It is, nevertheless, unlikely that this is the predominant factor, because, in the absence of more data, it seems probable that an effect due to this factor would not decrease with such relative rapidity at first, nor would it vary from cell to cell, as the ageing effect does in some cases (*e.g.*, compare cells having $\tau = 25$ and $\tau = 0{\cdot}50$ respectively).

(4) *Changes in concentration of the cadmium sulphate solution.*—This has been found to account satisfactorily for the major part of the ageing of *unsaturated* cells, but it is not apparent how this could possibly occur in the saturated cell with its excess of crystals and complete protection by " the paste."

(5) *Hydrolysis in the paste and transference phenomena.*—These phenomena have been the subject of study by numerous physical chemists, and a review of their results has suggested to us no known nor conceivable change which could account for the observed ageing phenomenon satisfactorily.

(6) *The results of drawing too much current; continued current leakage; polarization effects; gas accumulations.*—These various effects have been examined experimentally and do not produce the type of change required, even when considerably enhanced. The after-effects are all of short duration tending always to recovery with the exception of gas-accumulation on the "paste" side, which does not affect the e.m.f. observably.

(7) *Slow acidification.*—It is not apparent how slow acidification of the cell could take place, but if it did take place it might lead to the results observed, both in regard to manner and magnitude.

(8) *The slow solution of foreign ingredients.*—It remains to discuss what appears to us as the most probable cause of the ageing phenomenon, namely, the introduction of foreign ions from the glass by slow solution and diffusion. Solutes obtained from the glass would be dissolved very slowly for years, and only minute quantities would be involved in the whole process, which would approach a limit asymptotically. The analysis below shows that this leads to a prediction of cell behaviour of the type observed. Furthermore, the variation with different types of cell containers, and with the previous time of contact of the solution with glass containers, is consistent with our interpretation of the constant τ. The transformation of a fraction of one of the main ingredients as a result of the introduction of these new ingredients would lead again to changes in voltage proceeding in the same characteristic manner.

It is known, that under circumstances of this kind, the relation between change in e.m.f., e, and concentration c, would be given approximately by a relation of the type

$$e = a + b \log c.$$

The application to our problem, together with a reference to the significance of zero concentration, are outlined in detail below, in part (*b*) of this section.

(9) It is possible that slow changes in the state of the crystalline structure, or aggregation in the amalgam, might cause a slow change in electromotive force of the type observed. In this case the growth of the transformed part of the amalgam and its influence on the electromotive force would be amenable to the same analysis as that given below.

(*b*) *Quantitative development of theory, and practical formulæ.*

This phenomenon of "ageing" can be given a satisfactory and particularly useful theoretical treatment by assuming that the change in electromotive force is proportional to the logarithm of the concentration of some impurity or of some transformed part of an ingredient, as suggested in the preceding paragraphs. Let us call this quantity x, and note carefully, that it must necessarily be minute in magnitude and extremely slow in change, but that this slow change must be relatively rapid at first. The

suggestion that this quantity, x, comes from the glass seems probable; but whether this assumption is right or wrong, the value and practical use of the analysis should remain almost unimpaired, for the numerous observations are undoubtedly coordinated successfully by our equations. If this is not the correct explanation, then it must at least be of this type, and lead to similar expressions. The chemical changes are too small and too slow to be examined by a direct chemical investigation, but granting our assumptions, the theoretical analysis is in accordance with the principles and data of Physical Chemistry.

If the electromotive force, E, of the cell is equal to E_0, at construction, when $x = b$ (where $b >$ some small finite quantity), and if $E = E_F$ when $x = a$, where E_F is the final value to which it approaches asymptotically, we have,

$$E = E_0 + B \log_e x/b = E_F + B \log_e x/a.$$

Since E decreases with the growth of x, B is a negative constant, while $\log x/b$ is always positive, and $\log x/a$ always negative. It should also be observed that $dE/dx = B/x$ for $a > x > b$.*

The rate of accumulation of x in the cell will be given by

$$\frac{dx}{dt'} = k\,(a - x)$$

where a may be either the saturation value for x, or the total amount of x available for solution in the case where this total amount is less than the saturation concentration. It will be seen that $dx/dt' = 0$ when $x = a$ and $t' = \infty$.

It follows, therefore, on solving this equation, that

$$x = a\,(1 - e^{-kt'})$$

and if $t' = \tau$ when $x = b$, and if we measure t from this time when $E = E_0$, we have $t = t' - \tau$, and therefore,

$$x = a\left(1 - \frac{a - b}{a}\,e^{-kt}\right) = a\,(1 - e^{-k(t+\tau)}),$$

where

$$\tau = \frac{1}{k}\log_e \frac{a}{a - b} = -\frac{1}{k}\log_e\,(1 - e^{(E_0 - E_F)/B}).$$

* The impossible value $E = \infty$ for $x = 0$, does not occur, since $x > b$; but if we were interested in the possible meaning of the case $x = 0$, it would be seen (see expression for dE/dt) that at $x = 0$, $dE/dt = \infty$ as well as $dE/dx = \infty$, so that E at $x = 0$ cannot, owing to this instantaneous rush, be regarded as a real value; furthermore, a review of the formulæ of this type, involving the logarithm of the concentration will show that extrapolation to zero concentration is not permissible on other grounds. The growth of x is necessarily by finite increments and no change in E can take place until *after* the first small amount of x has appeared in the solution. The equations, therefore, *do not apply at all* until after x has a small finite value, ε, possibly of a molecular order; and ε may be much less than the b in our case; but if the solution were initially free from the material x, this quantity, ε, would serve as b in the equations,—the equations would only hold when $x \geqq \varepsilon$, and the upper limit to E would occur at this point and be equal to E_0.

Hence, substituting for x, in the expression for E, we have

$$E = E_0 + B \log_e \frac{1 - e^{-k(t+\tau)}}{1 - e^{-k\tau}} = E_F + B \log_e (1 - e^{-k(t+\tau)}),$$

and it also follows that

$$\frac{dE}{dt} = \frac{Bk}{e^{k(t+\tau)} - 1} = -\frac{Bk}{e^{(E_0 - E_F)/B}} (e^{(E_0 - E)/B} - e^{(E_0 - E_F)/B}) = Bk \frac{a - x}{x},$$

in which it can at once be verified that $E = E_0$ when $x = b$ and $t = o$; that $E = E_F$ when $x = a$ and $t = \infty$; and that $dE/dt = o$ when $E = E_F$. The latter necessary condition is not apparent in the useful approximate formula (derived below)

$$E = E_0 + B \log (t + \tau)/\tau,$$

which would appear to give $E = -\infty$ when $t = \infty$, instead of $E = E_F$.

The derivation of this useful approximate equation is simple; it can easily be shown that

$$E = E_0 + B \log_e \left\{ \left(\frac{t+\tau}{\tau}\right) \left(\frac{1 - \frac{k(t+\tau)}{2!} + \dots}{1 - \frac{k\tau}{2!} + \dots} \right) \right\}.$$

The experimental observations in the case of the cells recorded in figs. 1 and 2 show that kt and $k\tau$, and their higher powers, are so small ($\tau = 0{\cdot}75$ and $k < 0{\cdot}00059$) that they may be neglected in the series above, even when t is as large as 240 months, that is 20 years. Indeed the difference between the two formulæ would only be about 7 millionths of a volt if we imagined the cells to survive without other changes to the value $t = 1830$ months, that is after over 152 years. However, sufficient as this formula

$$E = E_0 + B \log_e \left(\frac{t+\tau}{\tau}\right) = E_{1-\tau} + B \log_e (t + \tau)$$

may be, for tracing the ageing for many years, it is useless for the estimation of k and E_F.

It is useful to note that the rate of ageing is given very closely by $dE/dt = B/(t + \tau)$, or from the more general expression we have

$$\frac{dE}{dt} = \frac{Bk}{e^{k(t+\tau)} - 1} = \frac{B}{(t + \tau)(1 + \frac{1}{2}k(t + \tau) + \dots)},$$

where $k(t + \tau)$ and higher powers may usually be neglected until t is large.

(*c*) *The ageing equation for dealing with the average electromotive force of a number of cells.*

If the ageing of each individual cell is given by an equation of the type

$$E_{1,M} = A_1 + B \log (M + \tau_1)$$

the ageing of the mean electromotive force, $\bar{E}_M$, of a group of n cells is given by

$$\bar{E}_M = \frac{E_1 + E_2 + \ldots + E_n}{n} = \bar{A} + \frac{B}{n} \log (M + \tau_1)(M + \tau_2) \ldots (M + \tau_n),$$

where $\bar{A} = (A_1 + A_2 + \ldots + A_n)/n$; and it should be observed that if this is put into the form

$$\bar{E}_n = \bar{A} + B \log (M + \bar{\tau})$$

it *cannot in general* be assumed that $\bar{\tau}$ is the mean of the τ's, or indeed that $\bar{\tau}$ could be any constant whatever. It can easily be shown, by equating the above expressions, that $\bar{\tau}$ involves M, and *if* M *is large*, is given by

$$\bar{\tau} = \frac{\tau_1 + \tau_2 + \ldots + \tau_n}{n} + \frac{(\tau_1 + \tau_2 + \ldots + \tau_n)^2 - n(\tau_1^2 + \tau_2^2 + \ldots + \tau_n^2)}{2n^2} \cdot \frac{1}{M} + (\text{terms involving higher powers of } 1/M),$$

and *if* M *is small*, $\bar{\tau}$ is given by

$$\bar{\tau} = (\tau_1 \tau_2 \ldots \tau_n)^{1/n} + \left\{ \frac{(\tau_1 \tau_2 \ldots \tau_n)^{1/n}}{n} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + \ldots + \frac{1}{\tau_n} \right) - 1 \right\} M + (\text{terms involving higher powers of M}).$$

An inspection of these expressions for $\bar{\tau}$ shows that we could use the arithmetical mean of the τ's for large values of M, and the geometrical mean * for small values of M, but for a general expression for the whole range, a very cumbersome formula is required, which would not in general lead to the useful linear graphs of the type shown in fig. 2 (except for large values of M).

If, however, the deviations of the various τ's from their mean value is small enough to render the difference between the arithmetical mean and the geometrical mean, a negligible quantity, then

$$\bar{E}_M = \bar{A} + B \log (M + \bar{\tau})$$

We see, therefore, that when averaging the e.m.f.'s of cells we must choose cells which have values of τ differing very slightly among themselves, that is if we desire to make ageing corrections or evaluate the constants with the highest precision attainable. In terms of our theory of the ageing, this means that the unavoidable impurity (or transformed ingredient) present at the time of construction must be approximately equal in concentration in each cell of the group. For the purpose of ordinary testing this means merely that during the first few years of ageing, we must not combine in one batch, cells which show marked differences in rates of ageing.

* The term geometrical mean is applied in its generalised sense, that is, the nth root of the product of n quantities.

These considerations apply equally to the evaluation of $\bar{\tau}$ in the more general expression

$$\bar{E}_t = \bar{A}' + B \log (1 - e^{-k(t+\bar{\tau})})$$

provided that k is sufficiently small.

A thorough investigation of the errors produced by variations in the choice of τ was made, and the following practical rule for rejection was followed when choosing a reference batch. *Reject any cell if the high value of its particular τ produces an error in the mean $\bar{E}_M$ of more than 1 microvolt at any part of the curve after two months, as a result of assuming $\bar{\tau}$ a constant.*

[To illustrate the importance of the above requirement, consider the simple case of only two cells, having equations, for example

$$E_M = 30 - 39{\cdot}4 \log_{10} (M + 1)$$

and

$$E_M = 50 - 39{\cdot}4 \log_{10} (M + 25),$$

The average value of E_M is given by

$$\bar{E}_M = 40 - 39{\cdot}4 \log_{10} \sqrt{(M + 1)(M + 25)}$$

and substitution will at once show that the choice of any one constant value for $\bar{\tau}$ in the expression

$$\bar{E}_M = 40 - 39{\cdot}4 \log_{10} (M + \bar{\tau})$$

will lead to appreciable errors. If $\bar{\tau} = 5$ months (the geometrical mean) is taken, the values for the first week and also *after* several years would be given correctly, but serious errors would arise in calculations for the first few years of the cells' lives. If $\bar{\tau} = 13$ months (the arithmetical mean) is chosen, the whole range of values during the early life of the cell would be incorrect.

If, however, we have two cells having equations, such as

$$E_M = 30 - 39{\cdot}4 \log_{10} (M + 1)$$
$$E_M = 50 - 39{\cdot}4 \log_{10} (M + 0{\cdot}75)$$

we may take either the arithmetical or the geometrical mean for $\bar{\tau}$, or indeed use either $\bar{\tau} = 1$ or $\bar{\tau} = 0{\cdot}75$ without seriously affecting any calculation of the ageing after a few months of age.]

This point has been discussed at length because, if care had not been taken in choosing cells having approximately the same value of τ, we should have failed to discover the formulæ which are found to give the ageing so accurately. As pointed out before, it is necessary to work with a batch rather than with individual cells in order to eliminate the possible errors of measurement (temperature effects, setting of potentiometer, etc.), so that *this stipulation that cells in a reference batch must have nearly equal values of τ (and thus nearly equal ageing coefficients at any given time), is one of fundamental importance, both in the practical application of the ageing correction, and in its determination.*

Section 4. The Numerical Evaluation of the Coefficients and Constants.

(*a*) *The Evaluation of B.*

As this constant has been found to be apparently the same for all neutral Weston Cells investigated at McGill, and as it determines the slope of the straight lines obtained when the useful method of plotting shown in fig. 2, is adopted, it is considered to be the most important constant in the ageing formulæ.

The following methods were used for evaluating it :—

(1) Since

$$E = E_F + B \log_e \{1 - e^{-k(t+\tau)}\},$$

we have

$$B = (E_1 - E_2) \Big/ \log_e \frac{1 - e^{-k(t_1+\tau)}}{1 - e^{-k(t_2+\tau)}},$$

where E_1 and E_2 are the values of the e.m.f. at any two times, t_1 and t_2 ; and this reduces to

$$B = (E_1 - E_2) \Big/ \log_e \frac{t_1 + \tau}{t_2 + \tau}$$

when k is small, or whenever we are justified in assuming $E = A + B \log (t + \tau)$.

If we use values of t_1 and t_2, which are large compared to τ, then we have

$$B = (E_1 - E_2)/\log_e (t_1/t_2)$$

under circumstances where

$$\log_e \left(1 + \frac{\tau}{t_1} - \frac{\tau}{t_2}\right) \quad \text{or} \quad \tau \left(\frac{1}{t_1} - \frac{1}{t_2}\right)$$

is negligibly small compared to $\log_e (t_1/t_2)$.

Now in the McGill laboratories new batches of cells of suitable calibre were made in 1908, 1909 and 1923. If a batch of the older cells and a batch of the newer cells are each chosen according to the same rules of selection, and the readings for the older cells expressed in terms of the readings for the newer cells at the later date, we may obtain numerous values for E_1, E_2, t_1 and t_2 for substitution in the formula above.

This method was applied to the cells used in connection with curve 1, fig. 1, and gave the following mean value,

$$B = -17{\cdot}2.$$

(2) If the various comparisons with the reference means in use at London and at Washington are used in the same way as new cells, we may get from the above formula in (1) a large number of determinations of B, but they will be subject to the limitations of these international comparisons (see Section 5). The majority of the determinations made in this way lie between $-16{\cdot}3$ and $-17{\cdot}7$, with a mean value of

$$B = -17{\cdot}1.$$

(3) For large values of t we should have $dE/d(\log t)$ approaching a constant value. If we arbitrarily adjust the reference mean so that readings for the 1923 cells (expressed in terms of the older cells) decrease with time in the same manner that the similar older cells did in 1908 and 1909, and then find that the successive means of the older cells lie on a smooth curve which is the obvious continuation of the early curve for the old cells, the procedure of adjustment is justified, particularly if the results coincide with those of independent methods.

This procedure was followed, and also gave consistent curves on plotting, which had constant values of $dE/d(\log t)$ for the old cells (that is, when these were referred to the new cells, the successive means for which were arbitrarily adjusted to give the same rates of ageing that the old cells had experienced in 1908 and 1909). Values of B obtained in this way ranged from $-16{\cdot}9$ to $-17{\cdot}6$ and gave a mean value of

$$B = -17{\cdot}0.$$

(4) If the particular cells which appear to remain with the highest values when expressed in terms of the remainder are assumed to be constant for a year or two, and temporarily taken as the reference mean, we may express new cells having rapid ageing, in terms of these constant cells for this period. We can then determine dE/dt for these curves, but we cannot proceed to large values of t in this case, and we must use τ in our calculations. (As we need B to get τ this would involve "reasoning in a circle," if it were not that B can be estimated by several independent methods, and τ does not need to be known accurately if it is small.)

Curves for dE/dt were obtained in this way, and in order to utilise the measurements fully, the method of finite differences and the standard interpolation formulæ were used; τ was obtained by the method outlined in (*b*) below, which required a previous approximate knowledge of B. This method of procedure gave four values of B, -16, -17, -18 and -16. It is not accurate, but is interesting as a confirmation.

(5) A reliable independent method requires the use of saturated acid cells. A picked batch of these acid cells was assumed to have negligible ageing during five years; this was justified by other comparisons, such as comparing acid cells differing in age by one year. These acid cells were used as a reference mean, and the ageing of both old and new neutral cells were plotted with reference to the steady acid cells. An analysis of these curves showed that they were again of the same form and as correct for the slowly ageing old cells as for the more rapidly ageing new cells. When B was determined from these curves the values ranged from $-16{\cdot}9$ to $-17{\cdot}5$ with a mean of

$$B = -17{\cdot}1.$$

The final mean adopted was $B = -17{\cdot}1$; this involved nearly 3000 readings, and

all the above methods. It is considered that B is probably constant for all the cells, and that the range of values obtained lies within the limits of error in estimation.

If the logarithms of the formulæ are expressed more conveniently to the base 10, then the corresponding constant, as used for example in fig. 2, is

$$B/\log_{10} e = -39{\cdot}4.$$

It should be pointed out that B cannot be determined accurately unless batches of at least five uniformly behaving cells are considered. It is also obvious that records of differences alone are inadequate; a definite reference mean must be recaptured independently on a number of occasions, otherwise by an arbitrary choice of reference means any curve might be fitted.

(*b*) *The Evaluation of* $\bar{\tau}$.

As pointed out in section 3 (*c*), the ageing formulæ cannot be applied accurately to a batch, for small values of t, unless it is known that the values of τ for the given cells, do not differ greatly. This can be assured by putting into one batch only cells which age in an approximately similar manner during their first few months.

Having ascertained B, there are two simple ways of evaluating τ for a given batch of similarly ageing cells.

(1) By using the expression

$$B = (E_1 - E_2)/\log \frac{t_1 + \bar{\tau}}{t_2 + \bar{\tau}},$$

in which one of t_1 and t_2 is small and the other is large, but each greater than τ. (If both t_1 and t_2 are large, $\bar{\tau}$ cannot be evaluated with sufficient accuracy, as it would be necessary in that event to know B and $(E_1 - E_2)$ to an accuracy which is unattainable; also if t_1 does not differ greatly from t_2, similar arithmetical limitations arise.)

Example.—(For batch similar to that giving curve 2, fig. 1.)

At $t_1 = 1$ month, $E_M = 20$ microvolts.
,, $t_2 = 240$ months, $E_M = -64{\cdot}5$ microvolts

therefore

$$-17{\cdot}1 = (20 + 64{\cdot}5)/\log_e \frac{1 + \bar{\tau}}{240 + \bar{\tau}},$$

or

$$-39{\cdot}4 = 84{\cdot}5/\log_{10} \frac{1 + \bar{\tau}}{240 + \bar{\tau}},$$

which gives

$$\bar{\tau} = 0{\cdot}73 \text{ month}.$$

Applying this method to the thirty cells represented by curve 2, fig. 1, a range of values was obtained, of which the majority lay between 0·65 and 0·85. This

discrepancy will be seen on inspection to be within the arithmetical limitations; it will also be observed that if $\bar{\tau}$ is of this order of magnitude, an error of 50 per cent. in $\bar{\tau}$ will have a negligible effect on the calculation of E_M when t is greater than 6 months. If $\bar{\tau}$ is large, for example 25, the importance of determining its magnitude more accurately is paramount, and in this case the above method is not sufficiently accurate for application to "young" cells.

The mean of the values of $\bar{\tau}$ for the case of the thirty cells represented by curve 2, fig. 1, was 0·74, and this figure is probably correct to within 0·05, as indicated by the results of the second method.

(2) Having determined B, and the value of the initial reference mean on various occasions, the slopes of the lines for all cells plotted according to the method of fig. 2, are known, that is if they follow our expression. If the values of E_M are plotted on this semi-logarithmic paper as though the abscissae were log t instead of log $(t + \tau)$ then a curve will be obtained which is below the expected straight line and apparently asymptotic to it for large values of t. Inspection will show that the addition of a constant to t will bring the curve approximately into coincidence with this straight line. If it is found that one constant will apply equally satisfactorily for any part of this logarithmic scale, and particularly at the beginning when the linear distance on the logarithmic scale is relatively large, a confirmation of the validity of the procedure is obtained, and also a value for the constant itself.

In all cases tried, it was found that the graph on this kind of logarithmic paper (fig. 2) could be converted into a straight line in this manner, and that all the straight lines had the same slope, defined by $dE/d\{\log(t + \tau)\} = B$, whatever the value of τ, that is, whatever the initial rate of ageing.

In this way, for example, we obtained

$$\bar{\tau} = 0{\cdot}75 \pm 0{\cdot}05 \text{ for curve 2, fig. 1.}$$

$$\text{and } \bar{\tau} = 0{\cdot}75 \pm 0{\cdot}25 \text{ for curve 1, fig. 1.}$$

In estimating the range, those readings which are obviously eccentric due to some other causes, are rejected, as for example at the right in graph 1, fig. 2, where the hysteresis of old cells increases the occurrence of erratic readings.

The effect on these calculations of variations in E_0 due to the use of different amalgams, or other causes, is negligible. As in the case of variations in $\bar{\tau}$, the straight lines plotted according to the method of fig. 2, are merely shifted parallel to themselves for various values of E_0. It will be observed that when E_0 (or E_1 on the log graph) changes, the abscissa is still log $(t + \tau)$, but if τ is changed, it will be noted that the abscissa unit is a new quantity, so a change in the initial E is not equivalent to a change in τ; this is very apparent if the changes are made in fig. 1 instead of in fig. 2.

(*c*) *The determination of* E_0, *in terms of the "Initial Reference Mean."*

The measurements of the e.m.f's of all cells are recorded finally as differences from the "initial reference mean" which we may call E_i. The absolute value of E_i is not known to the accuracy with which it can be reproduced, and therefore all our records are expressed as differences from it; in our opinion the average "international mean" is (as shown in Section 5, Table IV) equal to E_i. The determination of E_i on any given date involves the essential rules and procedures which are discussed in detail in Appendices A and B. Originally, however, we used a small set of reference cells having slow preliminary ageing, that is having high values of τ; this original reference batch corresponded very closely in e.m.f. with the international mean value.

An inspection of curve 2, fig. 2, shows that for those thirty cells, we have

$$E_{0.25} - E_i = 29{\cdot}5 \text{ microvolts}$$

and by producing the line back to the value 0·75 for (M + 0·75), that is for M = 0, we have

$$E_0 - E_i = 34{\cdot}4 \text{ microvolts}$$

for this batch of cells.

If some new reference mean were chosen which differed from ours by x microvolts, it would only be necessary to add $\pm x$ to each of our readings, or in other words to slide our ordinate scale up or down a distance x units.

It is instructive to show clearly the relations between the formulæ in a particular case, such as for these thirty cells.

We have

$$E_M = E - E_i = E - E_0 + 34{\cdot}4$$

where

$$E = E_0 + B \log_e \frac{1 - e^{-k(t+\tau)}}{1 - e^{-k\tau}},$$

and in this case where $\tau = 0{\cdot}75$, $B = -17{\cdot}1$, and $k = 0{\cdot}00058$, we have

$$E_M = 34{\cdot}4 - 17{\cdot}1 \log_e \frac{1 - e^{-{\cdot}00058(M+0{\cdot}75)}}{1 - e^{-{\cdot}00058(0{\cdot}75)}},$$

which reduces in the manner shown in Section 3 (*b*) to the simpler expression

$$E_M = 34{\cdot}4 - 17{\cdot}1 \log_e \left(\frac{M + 0{\cdot}75}{0{\cdot}75}\right),$$

$$= 29{\cdot}5 - 39{\cdot}4 \log_{10} (M + 0{\cdot}75),$$

as given in fig. 1.

(*d*) *The Determination of k and* E_F.

For the purpose of calculating the ageing it is not necessary to know the values of k and E_F, but it is of interest to consider them. Their significance depends on the validity of the theory which has been suggested for the ageing formula, and it should be noted that the new procedure for interpreting standard cells with increase in precision remains equally useful whether these two constants are correctly interpreted or not. To leave the work on an empirical basis, when a simple theory was available to account for the phenomena so consistently, seemed undesirable, but nevertheless it is important to distinguish between the constants which arise indisputably from the observations and these two which arise as a result of the theoretical treatment.

It will be observed that k and E_F cannot be calculated accurately from the available data, on account of the smallness of k, and the absence of information for the period when E would approach E_F, the final value. It is, however, possible to find an upper limit to k, and also to E_F from a consideration of the accuracy with which the formula fits the experimental results.

Let us suppose that at the time, t_r months, the approximate formula,

$$E = E_0 + B \log_e \{(t + \tau)/\tau\},$$

gives the value of E_r without doubt to within, say, σ microvolts, then

$$B \log_e \left(\frac{1 - e^{-k(t_r + \tau)}}{1 - e^{-k\tau}}\right) - B \log_e \left(\frac{t_r + \tau}{\tau}\right) \lessapprox \sigma,$$

that is

$$\log_e \left(\frac{\tau (1 - e^{-k(t_r + \tau)})}{(t_r + \tau)(1 - e^{-k\tau})}\right) \lessapprox \frac{\sigma}{B},$$

and knowing τ to be small in the case of fig. 1, we have, therefore, to a first approximation when t_r is large, that

$$k \lessapprox -\frac{2\sigma}{Bt_r}.$$

Now an inspection of fig. 2 (confirmed by similar records not submitted here) shows that up to $t = 200$ months, the curve given by the approximate formula is in general within one microvolt of the observed mean values for the cells, when expressed in terms of the McGILL initial reference mean. Since $B = -17{\cdot}1$, we have, therefore, for this batch of cells,

$$k \lessapprox -\frac{2 \times 1}{-17{\cdot}1 \times 200} \lessapprox 0{\cdot}000585.$$

It is possibly much less than this, but is certainly not greater.

Since $E_F - E_0 = -B \log_e (1 - e^{-k\tau})$ we have in the case when $\tau = 0{\cdot}75$ that $E_0 - E_F = 134$ microvolts, or more if $k < 0{\cdot}000585$. In the case of curve (2), in fig. 1, this would make the final value of the mean E_M for the thirty cells equal to -100 micro-

volts (or lower) when referred to our reference mean. Thus we may state confidently that this ageing effect in the thirty cells will continue until there has been a reduction in voltage of *at least* 134 microvolts below E_0 for these cells, that is, 100 microvolts below the McGILL initial reference mean. This would apply to the majority of those cells which have the "initial reference" value at the age of five months. If an undisturbed individual cell has a value, for example, of — 40 at the age of five months, then, *if* τ *is small* and if other factors remain negligible, we would expect it to decrease ultimately to at least — 140 microvolts below the reference mean; this limit would not, however, be approached within the observer's lifetime!

These approximate calculations for k and E_F obviously apply only to cells which experience no other forms of disturbance or degeneration, but any failure to take into account other ageing influences in no way affects the practical application of the approximate formula ($E_M = A + B \log (M + \tau)$ to cells which are less than twenty years old, provided always that they fulfil the selection requirements in regard to consistent behaviour.

SECTION 5.—INTERNATIONAL COMPARISONS OF STANDARD WESTON CELLS.

The repeated kindnesses and continued courtesy of the authorities at the National Physical Laboratory, Teddington, and at the Bureau of Standards, Washington, have made numerous comparisons possible. Formerly the McGill reference mean was corrected, each time a comparison was made, to agree with the results of the exchanges with these laboratories, but this procedure has been abandoned. It was found that the usual errors in a comparison performed with the aid of a small number of transported cells were greater than the errors which remain, if it is assumed that a large number of properly constructed cells, similarly selected, corrected for ageing, and kept at rest, should constitute the highest court of appeal on the question of reproducibility.

The development of a reliable "code" for the selection of reference cells from either new or old cells, and the discovery that the ageing of batches of cells could be evaluated with extraordinary precision, made it possible for us to maintain a uniform reference mean with an accuracy much greater than had apparently been achieved before. The procedure for this has already been reported, and involved (1) the construction of new cells at different dates, (2) the repeated comparisons of old and new cells, (3) the comparison of neutral cells with acid cells, and (4) the determination of the rates of ageing of reference batches.

As a result of this work it was most interesting to revise the old McGill records for international comparisons, and adopting a much less humble attitude, to express the London and the Washington mean values from time to time (as determined by the common method of transported cells) in terms of the initial McGill reference mean. This mean, it is claimed, is maintained to within one part in a million, being recaptured on any given date by means of the analysis for ageing without any reference

BLE IV.—International Comparisons of the "Reference Means" of London and Washingto
Reference Mean for Weston Standard Cells (1908–1928).

(Demonstrating also the accuracy obtainable in applying the ageing correction to

L = value of the National Physical Laboratory mean for neutral cells.
B = value of the Bureau of Standards mean for neutral cells.
Mc = value of the initial McGill reference mean for neutral cells.
X = value of the temporary McGill mean for a given date, uncorrected fo

All readings are in millionths of a volt.

Bureau of Standards and McGill.

Transportation of Cells.	Cell Label.	Observations at Bureau of Standards.		Observations at McGill.		Mc − X on given date (taken from ageing curves) (*d*).	X + *m* = Mc + *m* − *d*.	Approx. ageing corrections for interval between observations (*a*).	d fr
		Date of Obs.	Obs. (B + *b*)	Date of Obs.	Obs. (X + *m*)				
From B. of S. to McGill (July, 1908)	III	July 20–22, 1908	B + 3	Jan. 8–9, 1909	X + 4	+ 6	Mc − 2	5	
	IV		B + 2		X + 4		Mc − 2	5	
	VI		B + 36		X + 37		Mc + 31	6	
From McGill (April, 1909) to B. of S.	A	April 26–29, 1909	B + 1	April 23, 1909	X + 8	+ 10	Mc − 2	0	
	C2		B − 12		X − 5		Mc − 15	0	
	VI		B + 28		X + 37		Mc − 27	0	
From B. of S. (April, 1909) to McGill	A	April 26–29, 1909	B + 1	May 4–5, 1909	X + 10	+ 10	Mc + 0	0	
	C2		B − 12		X − 8		Mc − 18	0	
	VI		B + 28		X + 40		Mc + 30	0	
From B. of S. (Oct., 1918) to McGill	197	Oct., 1918	B − 61	Jan. 29–Feb. 21, 1919	X − 8	+ 54	Mc − 62	0	
	201		B − 48		X + 14		Mc − 68	0	
From McGill (May, 1919) to B. of S.	197	July 24, 1919	B − 53	May 2, 1919	X + 6	+ 55	Mc − 49	0	
	201		B − 42		X + 8		Mc − 47	0	
) From McGill (Dec., 1924) to B. of S.	61	Jan. 5—6, 1925	B + 6	Dec. 16–23, 1924	X + 62	+ 59	Mc + 3	− 2	
	65		B + 4		X + 59		Mc + 0	− 2	
	84		B − 64		X − 11		Mc − 70	0	
) From McGill (Oct., 1925) to B. of S.	62	Nov. 18, 1925	B − 18	Oct. 16–24, 1925	X + 56	+ 61	Mc − 5	− 4	
	83		B − 61		X − 5		Mc − 66	0	
) From B. of S. (Oct., 1925) to McGill	197	No record received	?	Feb., 1927	X + 7	+ 61	Mc − 54	0	
	563		?		X + 35		Mc − 26	...	
	564		?		(Erratic)			...	

shington in Terms of the McGill

ction to old cells.)

cells.

ected for ageing.

ox. ng tions r val een va- ns).	B − Mc = m − d − b + a.		
	As deduced from each cell.	Mean value of B − Mc in microvolts.	Error due to shaking, etc., etc. probably less than
5	+ 0	+ 1	(± 1)
5	+ 1		
5	+ 1		
)	− 3	− 2	(± 2)
)	− 3		
)	− 1		
)	− 1	− 2	(± 2)
)	− 6		
)	+ 2		
)	− 1	+ 4	(± 4)
)	+ 8		
)	+ 4	+ 0	(± 4)
)	− 5		
2	− 5	− 6	(± 2)
2	− 6		
)	− 6		
4	+ 9	+ 2	(± 7)
)	− 5		
)	0 ?	Compare this with B − 53 in (9) above	...
.	...		
	...		

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1925) to McGill	563	received	?		X + 35	+ 61	Mc — 26	...	
	564		?		(Erratic)		...	...	
) From B. of S. (Oct., 1928) to McGill	61	Oct. 2, 1928	B — 32	Dec., 12, 1928	X + 38	+ 65	Mc — 27	0	
	62		B — 64		X + 3		Mc — 62	0	
	65		B — 63		(Erratic)		...	0	
	83		B — 64		X — 4		Mc — 69	0	
	84		B — 64		X + 1		Mc — 64	0	

National Physical Laboratory and McGill.

Transportation of Cells.	Cell Label.	Observations at the Nat. Phys. Lab.		Observations at McGill.		Mc — X on given date (Taken from ageing curves) (*d*).	(Mc + *m* — *d*)	Approx. ageing corrections for interval between observations. (*a*)	d fr
		Date of Obs.	Obs. (L + *l*).	Date of Obs.	Obs. (X + *m*).				
) From N.P.L. (Jan., 1909) to McGill	S17	Jan., 1909	L + 0	Feb. 18–Mar. 9, 1909	X + 3	+ 8	Mc — 5	2	
	S20		L + 0		X + 3		Mc — 5	2	
	S21		L + 0		X + 3		Mc — 5	2	
) From N.P.L. (April, 1909) to McGill	M10	April, 1909	L — 5	May 21–25, 1909	X — 3	+ 11	Mc — 14	2	
	M11		L — 5		X + 9		Mc — 2	2	
) From McGill (Sept., 1911) to N.P.L.	0	Dec. 22–Jan. 19, 1911–12	L — 27	Sept. 14, 1911	X + 9	+ 36	Mc — 27	— 2	
	Q5		L — 21		X + 11		Mc — 25	— 2	
	C3		L — 31		X + 17		Mc — 19	— 3	
) From N.P.L. (June, 1912) to McGill	1·6	June, 1912	L — 10	July 29–Sept. 5, 1912	X + 32	+ 40	Mc — 8	0	
	1·8		L — 10		X + 44		Mc + 4	0	
0) From McGill (Sept., 1923) to N.P.L.	54	Nov. 21–Dec. 9, 1923	L — 68	Sept. 17–20, 1923	X — 6	+ 59	Mc — 65	0	
	55		L — 65		X — 5		Mc — 64	0	
	81		L — 69		X — 10		Mc — 69	0	

.	...	this with B — 53 in (9) above	...
.	...		
)	+ 5	+ *0*	(± 3)
)	+ 2		
)	...		
)	— 5		
)	+ 0		

rox. ing ctions or rval veen rva- ns. *b*)	L — Mc = *m* — *d* — *l* + *a*.		
	As deduced from each cell.	Mean value of B — Mc in microvolts.	Error due to shaking, etc., etc. probably less than
2	— 3	— *3*	(± 2)
2	— 3		
2	— 3		
2	— 7	— *1*	(± 5)
2	+ 5		
2	— 2	+ *0*	(± 4)
2	— 6		
3	+ 9		
0	+ 2	+ *8*	(± 5)
0	+ 14		
0	+ 3	+ *1*	(± 2)
0	+ 1		
0	+ 0		

whatever to the results of the exchanges themselves, and without assuming that any exceptional cells with minimum ageing could be identified with certainty and taken as constant.

It must be observed that although any one definite mean value can now be recaptured to within one or two millionths of a volt on a subsequent date, and the mean of any given batch referred to it—it is not possible with this degree of accuracy to estimate the mean value for a particular group of cells at the moment of construction. Contrary to former ideas, older cells chosen properly can be evaluated in advance, more accurately than new cells, even if the new cells have slower ageing rates. This is also evident from the formulæ for ageing; the differences in τ obviously lead to greater uncertainties in deducing the early averages than in determining the average mean value of cells several months old.

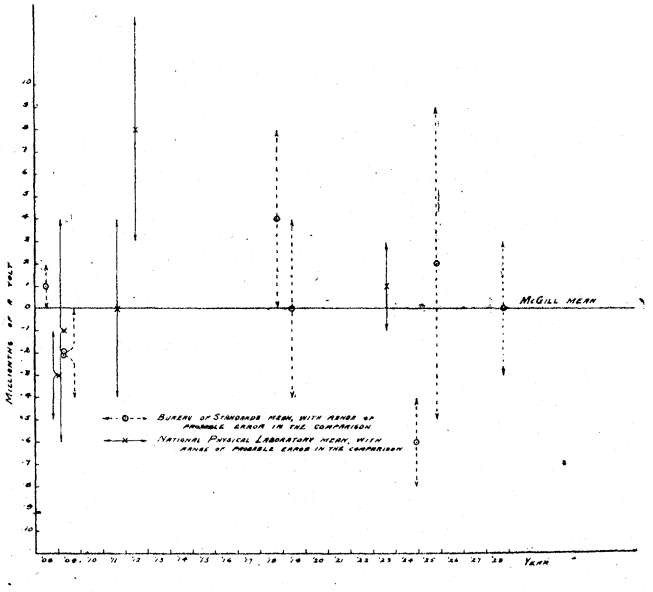

FIG. 6.—International Comparisons with the McGill Reference Mean for Neutral Weston Cells (1908-1928).

When the former comparisons with London and Washington cells were re-expressed in terms of the McGill initial reference mean, it was surprising to find not only that the calculated average differences were reduced in magnitude, but that the differences between London and Washington were less than we had estimated before. The results of this analysis are shown in Table IV and fig. 6.

It is obvious that the apparent international divergences indicated by these data may be due, (1) to the changes in the cells that are transported, (2) to the fluctuations of a few microvolts, often apparent under ordinary circumstances in cells kept at rest, when only two or three cells are used, (3) to the limitations of the methods of measurement when only a few readings are averaged, (4) to the temporary changes in the

estimate of the reference mean at the laboratories compared—but *very probably not* due to real divergences between similar batches of cells beyond 3 or 4 millionths of a volt at the most. It is thought that if the other laboratories had determined their " means " by calculating the average ageing of an average batch rather than by endeavouring to eliminate this correction by the repeated choice of cells with negligible ageing (that is with high values of τ), that the real differences could have been shown to be within one part in a million.

If an analysis of the McGill comparisons is made as formerly without correct reference to the ageing of our standard batches, but solely by the aid of new cells and exchange cells, the agreements are such that the international differences appear on occasion to be as high as 10 and 15 microvolts instead of only 2 or 3, as indicated in fig. 6, when these new methods are used.

It is remarkable to note that our average difference from Washington for eight exchanges during twenty years is zero, and the greatest divergence is only 6 microvolts, while our difference from London for five exchanges is 1 microvolt, with a maximum of 8.

If ageing is ignored it is considered that, with a large number of cells to choose from, the same reference mean may be maintained to within 5, or at most 10, microvolts for many years, but with a limited number of cells it appears likely that a divergence of over 10 microvolts can easily develop. If, however, the ageing of the cells has been determined, it is clear that a larger fraction of available cells may be used, and with only two or three batches of ten cells each it is possible to maintain a reference mean for many years to within a millionth of a volt. (If this were not true then the divergences of observations from our ageing curves would have been increased by amounts equal to the fluctuations of the calculated reference mean; either the curves would not have been smooth or the same reference mean could not have been deduced to within one part in a million from batches of different types with different rates of ageing).

As it appears that acid cells " age " much less rapidly, it is recommended that they should be used in conjunction with neutral cells, taking into account their lower e.m.f. It should be noted, however, that acid cells appear to have a shorter life than neutral cells, and that a larger proportion of them have to be rejected on account of erratic behaviour; if these objections can be removed, they should replace the neutral cell entirely. (This last statement must be regarded as tentative, as our own experience has been limited to only twenty acid cells.)

In Table IV the headings are self-explanatory. The column for $Mc - X = d$ is the most important new feature, and is derived from curves such as those in figs. 1 and 2. Our reference batches did not differ in behaviour very much from that indicated by the mean curve, number 2, for thirty cells, and the figures in this column for $Mc - X$ may be checked very approximately by using that curve. Actually different batches were used on different occasions and their ageing curves varied, but few of them differed as much as curve 1 differs from curve 2 in figs. 1 and 2. It is conjectured that the

steady reference cells used for so long at the Bureau of Standards probably have curves of the type represented by curves 1 and 2 in fig. 3 (that is with high values of τ), but we had so few of this slowly ageing type that we found it more convenient to use cells with small values of τ, and, having determined their equations, we felt that no accuracy was lost by using them.

The last column in the table is obtained by observing the behaviour of the cells after transportations, and is rather an arbitrary guess. The agreement from one date to another appears to justify the limits given. In addition to this error there is the possibility of errors in measurement extending over several days, on account of the hysteresis of cells when the temperature regulation has been imperfect, or when too much current has been drawn from the cell, accidentally.

Our measurements are all made by measuring the differences of two cells, opposing one another, on a potentiometer wire along which there is a fall in potential of 1 microvolt per millimetre. In this way the differences between the cells can be measured with relatively crude apparatus to within a few parts in a thousand. If we know that a given difference is 10 microvolts, an uncertainty of 5 per cent. in this would not matter; so the difficult technique for potentiometer measurements to one part in a million, is by this measurement of differences always avoided in estimating reference means. If the full voltage of a single cell is to be used in a potentiometer measurement with the highest accuracy, we use either the Kelvin-Varley Slide specially calibrated,* or a high precision potentiometer kindly donated to us by the Eppley Institute. These are, however, inappropriate for the determination of the reference mean to one part in a million.

It must not be forgotten that it is quite common for a single good cell to fluctuate occasionally through 5 or 10 microvolts as a result of some unknown disturbance, see fig. 5. The foregoing type of analysis to one or two parts in a million is only possible when at least two or three batches of ten cells each are used, in order that these individual eccentricities may be eliminated. If cells are used freely, that is without special precautions, the attainable accuracy degenerates to several parts in a hundred thousand, which is indeed still a high precision for the majority of purposes.

APPENDIX A.

The Choice and Interpretation of Reference Batches.

As numerous inquiries have been received about the details of choosing a reference batch, the following report is submitted. It also includes further evidence of the validity and applicability of the ageing corrections. The rules which are given have been

* A. N. Shaw, "On the Use of the Kelvin-Varley Slide Potentiometer," 'Trans. Roy. Soc., Canada,' vol. 8, sect. 3, pp. 89–103 (1914).

adopted because they are found to lead to these consistent results of much higher precision than was formerly attained; but, doubtless, there are untried variations which might lead to equally satisfactory results, so while it is felt that the use of these rules has led to a marked improvement in precision, no claim of finality is made for them.

It is usually required *first* to choose an appropriate reference batch, and *then* to be able to refer it (and through it, all other cells) to the initial permanent reference mean adopted. The actual choice and procedure of interpretation is discussed in this appendix, and the method of effecting the calculation of the initial permanent reference mean, from the reading of the batch chosen, using the ageing corrections, is discussed separately in Appendix B. If these two procedures are not kept separate, confusion may easily arise, either in applying the methods or in checking the results.

(*a*) *The size and composition of a reference batch.*

Choose at least ten normal neutral cells of approximately the same age in months* and (as far as can be determined from a consideration of previous records) also of approximately the same rate of ageing, that is, decrease of e.m.f. with time. These cells should preferably be made according to standard specifications, but may have slight modifications if the effect of these modifications on the e.m.f. is definitely known. Each cell in the batch should be in the same kind of glass container, and should have been constructed at about the same speed of preparation.

There should not be more than four cells in the group made from the same supply of prepared ingredients, unless the batch as a whole can be compared with the other batches in order that the possibility of changes in e.m.f., due to defective chemical preparation or impurities, may be eliminated with certainty.

All cells should be rejected from the batch which do not fulfil the requirements for constancy given in (*b*) below; if possible these should be replaced by other cells which meet these requirements. Although five or six cells may often be adequate, it is generally advisable to maintain ten cells in order to have a reliable reference batch. It has been observed that a batch much larger will in general lead to no further increase in precision, under the existing methods of measurement and interpretation.

In a properly chosen batch of cells less than five years old, the average deviation of the e.m.f.'s of single cells from the mean of the batch should never exceed 20 microvolts, and the maximum difference of any one cell from the mean e.m.f. of the batch should never exceed 30 microvolts. With older cells, having long records available for analysis for the ageing corrections, larger variations than these may conveniently be admitted, if there is a shortage of cells.

* This is not necessary if the separate ageing corrections can be determined from available records with sufficient accuracy. Ordinarily, it is advisable to avoid the analysis of records necessary to differentiate between cells of different ages and with different values of τ, and if only a few cells are available it might be impossible to do this satisfactorily owing to the range of fluctuations due to other causes, found in the records of any one cell.

(*b*) *The rejection of unsatisfactory cells.*

Reject all cells younger than three months (unless it is possible by comparison with other accepted batches over a period of time, to determine that the variations in the ageing corrections, customary in young cells, are negligible in the given case, as for example is the case when the cells have high values of τ).

Reject any cell which has increased or decreased its deviation from the mean e.m.f. of the batch by 10 microvolts or more during the preceding two weeks. It is important to be sure that it is the cell which is at fault and not the temperature regulation of the bath in the vicinity of the cell.

Reject any cell which has a deviation from the mean e.m.f. of the batch greater than $10 + d$, where d is the mean deviation of the cells of the batch. In the case of cells five years or more in age, the limit $20 + d$ may usually be used safely; the divergences are greater in the older cells and the supply of cells may be limited, but the previous records are longer and lead to greater assurance in calculating corrections.

(*c*) *Examples of application of rules of selection.*

TABLE V.

Example 1—Cells from Different Laboratories. (The figures are differences in microvolts.) (25·00° C.) Readings taken in February, 1909.

Cells.	II.	III.	IV.	V.	XX.	A.	B.	S 17.	S 20.	S 21.	Mean e.m.f. of batch.	Mean deviation.
Given measurements of E.M.F. in terms of Cell XX	+ 20	+ 19	+ 21	+ 23	+ 0	+ 21	+ 25	+ 13	+ 14	+ 12	+ 17	—
Deviation from mean	3	2	4	6	*17*	4	8	4	3	5	—	6
With Cell XX rejected by rule	+ 20	+ 19	+ 21	+ 23	—	+ 21	+ 25	+ 13	+ 14	+ 12	+ 19	—
New deviation from mean	1	0	2	4	—	2	6	6	5	7	—	4
E.M.F. in terms of mean of batch. (Subtract 19 from first row of figures.)	+ 1	+ 0	+ 2	+ 4	(— *19*)	+ 2	+ 6	— 6	— 5	— 7	—	—
Final values referred to permanent reference mean*	— 1	— 2	0	+ 2	(— 21)	+ 0	+ 4	— 8	— 7	— 9	—	—

* Using average ageing correction, see Appendix B.

In the above table it will be seen that the given measurements consist in a record of the differences in microvolts between each cell in the batch and one of them chosen arbitrarily, as reference cell, usually for convenience the one of lowest e.m.f. A calculation of the deviation shows that Cell XX must, according to rule, be rejected. With this cell rejected, the mean reading of the remainder of the batch becomes + 19 instead of + 17 as before the rejection. Hence in order to express the e.m.f.'s as differences from the mean of the approved nine cells, it is necessary to subtract 19 from each original measurement.

A new cell meeting the requirements should now be included instead of XX if it is desired to follow the rules implicitly. As the mean deviation is less than 5, this would however make no difference in this case.

When the mean of the batch has been referred to the permanent initial reference mean with the aid of the average ageing correction (see Appendix B), or by comparison with other batches of known value, it is merely necessary to subtract the correction.

Table VI.

Example 2 :—A batch of thirteen high-grade cells including four used in Table V. The readings were taken in November, 1909, and are differences in microvolts at 25·00° C.

Cells.	D.	N.	O.	Q 1.	Q 2.	Q 3.	Q 4.	Q 5.	Q 6.	III.	IV.	A.	B.	Mean e.m.f. of batch.	Mean deviation.
Given measurements of e.m.f. in terms of Cell Q 6	+31	+38	+37	+28	+23	+7	+41	+43	+0	+36	+16	+38	+40	+29	—
Deviation from mean . . .	2	9	8	1	6	*22*	12	14	*29*	7	13	9	11	—	11
With Cells Q 6 and Q 3 rejected by rule	+31	+38	+37	+28	+23	—	+41	+43	—	+36	+16	+38	+40	+34	—
New deviation from mean . .	3	4	3	6	11	—	7	9	—	2	18	4	6	—	7
E.M.F. in terms of mean of batch. (Subtract 34 from first row of figures.)	−3	+4	+3	−6	−11	(−27)	+7	+9	(−34)	+2	−18	+4	+6	—	—
Final values referred to permanent reference mean*	−8	−1	−2	−11	−16	(−32)	+2	+4	(−39)	−3	−23	−1	+1	—	—

* The above cells are also described in the paper by Bronson and Shaw (*loc. cit.*) and with the exceptions of Cells III and IV were made at McGill. The general procedure will be seen to be the same as that discussed in example 1. See Appendix B for the derivation of the last row by means of the ageing correction.

from each final reading above, in order to refer each cell to the permanent initial reference mean.

The above group was chosen to include cells from quite different sources. S 17, S 20 and S 21 were made at the National Physical Laboratory at Teddington, and may have been over a year older than the others, but their rate of ageing was such that the use of the average ageing was adequate. Cells II, III, IV, V were made at the Bureau of Standards in Washington by H. L. Bronson. Cells A and B were made at McGill by A. N. Shaw, and Cell XX was a cell the history of which has been lost. The readings were made at McGill, at 25·00° C, with the exception of Cells II and V, which were read at the Bureau of Standards and expressed in terms of Cell XX by means of comparisons before and after the transportation of cells. Reference to Table IV illustrates the closeness of the comparisons; see cases (1), (2), (3), (4), (5) in that table, and for further data about the cells see the paper by Bronson and Shaw (*loc. cit.*).

The general requirements as to previous constancy, etc., were fulfilled.

Table VII.

Example 3 :—Twelve cells made independently in August, 1923, with new equipment and supplies. The readings were taken in May, 1924. (The figures are differences in microvolts.) (25·00° C.)

Cells.	60.	61.	62.	63.	64.	65.	66.	67.	68.	69.	70.	71.	Mean e.m.f. of batch.	Mean deviation.
Given measurements of e.m.f. in terms of Cell 70	+58	+68	+67	+69	+68	+68	+65	+66	+68	+123	+0	+66	+66	—
Deviation from mean	8	2	1	3	2	2	1	0	2	*57*	*66*	0	—	12
With Cells 69 and 70 rejected by rule	+58	+68	+67	+69	+68	+68	+65	+66	+68	—	—	+66	+66	—
New deviation from mean .	8	2	1	3	2	2	1	0	2	—	—	0	—	2
E.M.F. in terms of mean of batch. (Subtract 66 from first row of figures.)	−8	+2	+1	+3	+2	+2	−1	+0	+2	(+57)	(−66)	+0	—	—
Final values referred to permanent reference mean*	−4	+6	+5	+7	+6	+6	+3	+4	+6	(+61)	(−62)	+4	—	—

* These cells were made independently by one of the authors (R. J. C.) with different equipment and supplies and are, as before, all neutral cells. The general requirements as to relative constancy have been fulfilled. In Appendix B it will be seen why the ageing correction is plus in this case.

Table VIII.

Example 4:—A batch of ten cells, each five years old, illustrating a case where the ageing correction is important. The readings were taken in July, 1928, and are, as before, differences in microvolts at 25·00° C.

Cells.	60.	63.	64.	66.	67.	68.	69.	71.	78.	79.	Mean e.m.f. of batch.	Mean deviation.
Given measurements of E.M.F. in terms of Cell 60	0	+ 45	+ 82	+ 40	+ 61	+ 38	+ 61	+ 35	+ 50	+ 39	*+ 45*	—
Deviation from mean	*45*	0	*37*	5	16	7	16	10	5	6	—	15
With Cells 60 and 64 rejected	—	+ 45	—	+ 40	+ 61	+ 38	+ 61	+ 35	+ 50	+ 39	*+ 46*	—
New deviation from mean	—	1	—	6	15	8	15	11	4	7	—	8
E.M.F. in terms of mean of batch. (Subtract 46 from first row of figures.)	(— 46)	— 1	(+ 36)	— 6	+ 15	— 8	+ 15	— 11	+ 4	— 7	—	—
Value in terms of permanent reference mean*	(— 74)	— 29	(+ 8)	— 34	— 13	— 36	— 13	— 39	— 24	— 35	—	—

* The determination of the ageing correction — 28 for this case is discussed in Appendix B. Striking confirmation of the validity of the last row lies in the fact that if these cells are expressed in terms of other batches having different ages and corrections, the same figures are obtained independently for these cells. This was done with two other batches analysed separately and further confirmation was obtained by referring them to the acid cells (rated by independent estimates at an average of — 66) in which case there was a discrepancy of only 1 microvolt in the figures for the last row of the above table. Reference to Table IV shows further confirmation of a less exact character.

TABLE IX.

Example 5 :—A batch of ten cells each nearly 20 years old (averaging 230 months each) illustrating a case where the ageing correction is important. The readings are the mean for September, 1927, and represent differences in microvolts at 25·00° C.

Cells.	IV.	VI.	A.	B.	C_2.	C_5.	N.	Q_3.	S 20.	1·8.	Mean e.m.f. of batch.	Mean deviation.
Given measurements in terms of Cell B	+ 68	+ 92	+ 89	+ 0	+100	+ 22	+ 74	+ 51	+ 44	+103	+ 64	—
Deviation from mean	4	28	25	*64*	36	42	10	13	20	39	—	28
With Cell B rejected by rule	+ 68	+ 92	+ 89	—	+100	+ 22	+ 74	+ 51	+ 44	+103	+ 71	—
New deviation from mean	3	21	18	—	29	*49*	3	20	27	32	—	22
With Cell C_5 rejected by rule	+ 68	+ 92	+ 89	—	+100	—	+ 74	+ 51	+ 44	+103	+ 78	—
New deviation from mean	10	14	11	—	22	—	4	27	34	25	—	18
E.M.F. in terms of mean of corrected batch. (Subtract 78 from first row of figures.)	— 10	+ 14	+ 11	(— 78)	+ 22	(— 56)	— 4	— 27	— 34	+ 25	—	—
Value in terms of initial permanent reference mean. (Subtract 45.)*	— 55	— 31	— 34	(— 123)	— 23	(—101)	— 49	— 72	— 79	— 20	—	—
Values deduced from newer batches*	— 52	— 28	— 31	(— 120)	— 20	(— 98)	— 46	— 69	— 76	— 17	—	—

* Here again the procedure is apparent and the ageing correction is obtained as in Appendix B. Relying on the very old cells of this batch alone, and using the ageing correction, it will be seen that an error of only 3 microvolts is made, the last row indicating the values duduced with the aid of more reliable batches. An inspection of the figures will show that greater variations than 3 microvolts could arise in the use of small batches of cells as old as this, but in our collection these were the only ones which fulfilled the requirements at this age.

APPENDIX B.

THE RECAPTURE OF A FORMER REFERENCE MEAN.

It will simplify the explanation of the procedure if we consider first the analysis of a particular set of ideal readings. In Table X, in order to avoid the confusing additional corrections for the reduction of readings to what they would have been at a common

age, the cells and readings are imaginary cases, arranged to illustrate the points under discussion, but they are deduced from actual readings. In our records there were not available on any single date many groups of cells of the same age but of different types, because our batches were constructed in small numbers at different times, one or two groups only being made at a time. It was, however, nearly always possible by comparisons between batches and by interpolation to deduce very approximately what a given group would have read on some chosen date on which readings were not available. The validity of these indirect readings was always checked by deducing in turn with their aid and other readings, what the readings would be on some other occasion when readings all round were available for verification.

The batch marked (1) to (10) in Table X corresponds in behaviour to cells yielding an ageing graph like curve 1, fig. 1. The readings resemble and are based on those of

TABLE X.—Illustration of Method of Referring to Initial Reference Mean on Different Dates.

	Date I. Cells 2 months old.			Date II. Cells 14 months old.			Date III. Cells 62 months old.		
Cell.	1. As taken, referred to Cell Z.	2. Referred to mean of batch (1)–(10).	3. Referred to initial reference mean.	1. As taken, referred to Cell Z.	2. Referred to mean of batch (1)–(10).	3. Referred to initial reference mean.	1. As taken, referred to Cell Z.	2. Referred to mean of batch (1)–(10).	3. Referred to initial reference mean.
(1)	*— 11*	+ 2	+ 23	*— 7*	+ 4	— 4	*— 3*	+ 7	— 27
(2)	*— 16*	— 3	+ 18	*— 18*	— 7	— 15	*— 22*	— 12	— 46
(3)	*— 7*	+ 6	+ 27	*— 10*	+ 1	— 7	*— 20*	— 10	— 44
(4)	*— 14*	— 1	+ 20	*— 12*	— 1	— 9	*— 8*	+ 2	— 32
(5)	*— 15*	— 2	+ 19	*— 10*	+ 1	— 7	*— 2*	+ 8	— 26
(6)	*— 6*	+ 7	+ 28	*— 3*	+ 8	+ 0	*— 3*	+ 7	— 27
(7)	*— 21*	— 8	+ 13	*— 14*	— 3	— 11	*— 18*	— 8	— 42
(8)	*— 17*	— 4	+ 17	*— 18*	— 7	— 15	*— 10*	+ 0	— 34
(9)	*— 10*	+ 3	+ 24	*— 7*	+ 4	— 4	*— 1*	+ 9	— 25
(10)	*— 14*	— 1	+ 20	*— 11*	+ 0	— 8	*— 16*	— 6	— 40
(P)	*— 32*	— 19	+ 2	*— 9*	+ 2	— 6	*+ 4*	+ 14	— 20
(Q)	*— 35*	— 22	— 1	*— 10*	+ 1	— 7	*— 2*	+ 8	— 26
(Y)	*+ 3*	+ 16	+ 37	*+ 2*	+ 13	+ 5	*— 5*	+ 5	— 29
(Z)	*(R)+ 0*	+ 13	+ 34	*(R)+ 0*	+ 11	+ 3	*(R)+0*	+ 10	— 24
(A 1)	*— 100*	— 87	— 66*	*— 69*	— 58	— 66*	*— 45*	— 35	— 69*
(A 2)	*— 100*	— 87	— 66	*— 70*	— 59	— 67	*— 45*	— 35	— 69
(A 3)	*— 99*	— 86	— 65	*— 71*	— 60	— 68	*— 49*	— 39	— 73
Correction applied to get columns above	—	+ 13	+ 13+21	—	+ 11	+11 —8	—	+ 10	+10 —34

* N.B.—Note the agreement of the acid cells in the third columns.

actual cells, in magnitude, in ageing and in distribution of deviations. The equation for their ageing would be $E_M = 38{\cdot}0 - 39{\cdot}4 \log_{10} (M + 0{\cdot}75)$.

The cells (P) and (Q) correspond to cells which would have an equation $E_M = 53{\cdot}0 - 39{\cdot}4 \log_{10} (M + 20{\cdot}0)$; the cells (Y) and (Z) correspond to cells which would have an equation $E_M = 48{\cdot}0 - 39{\cdot}4 \log_{10} (M + 0{\cdot}25)$; and (A 1), (A 2), (A 3) correspond to readings of modern acid cells.

Consider the problem for the cell observer who has before him the sets of observations given in each of the three first columns with reference to Cell Z. Assume that he has chosen the batch (1) to (10) according to the rules given in Appendix A, except that the cells are only two months old in the case of the first date. Averaging for this batch it is apparent that he must add 13, 11 and 10, respectively, to obtain the three second columns for each date. Without further data about ageing, or without measurements of other cells, he would have no knowledge of how the absolute means might have changed between the dates, and, under such circumstances in the past, observers were sometimes tempted to accept the illusion of constancy. However, the readings for other cells such as P, Q, Y, Z, A 1, A 2, A 3, which vary systematically themselves, reveal the need for a permanent reference mean. The main problem is, therefore, how to recapture a given reference mean based possibly on other cells and determined at another date, and then to express the present readings in terms of it.

A simple approximation is at once possible if he has readings for reliable acid cells. He may assume that the average of the acid cells is steady and should read — 66 for several years. If so, he adds or subtracts the necessary figure to make this hold and would obtain a close approximation to the figures of the third columns in Table X; it will be seen that for date I they would be as given, for date II they would be 1 microvolt higher, and for date III they would be 4 microvolts higher than those listed. He may, further, allow for the ageing of acid cells at a rate of about 1 microvolt per annum, and make a still closer agreement. But he may not be sure of his acid cells, he may have no readings for acid cells on the dates in which he is interested, or the reference mean (possibly linking with an old important measurement) he desires to recapture may have been fixed before acid cells were developed. Furthermore it should be noted that for greater ages a large fraction of acid cells develop high resistance and lose their earlier remarkable constancy. What then has to be done, in the absence of acid cells or other batches of known e.m.f., in order to obtain the third columns ?

Other records must be consulted in which at least some of the cells of the batch have been compared with cells of known rating; these other cells may be such as those represented in the graphs of fig. 1, or they may be acid cells, or they may be sets of new cells. The record of the batch during an early period of its history and when it could be referred to some constant reference mean, is plotted on semi-logarithmic paper such as that of fig. 2 and by trial and error, a value of τ can be found which will make the graph a straight line as in fig. 2, and of the same slope, because the constant B is assumed universal for neutral cells. It is now necessary to know where the graph

really lies; it has, as it were, to be slid up or down parallel to the fixed slope. This is equivalent to finding the magnitude of $E_{1-\tau} - E_i$, that is, where the graph will cut the ordinate axis in fig. 2. (For example, in curve 2, fig. 2, $E_{1-\tau} - E_i = E_{0\cdot25} - E_i = 29\cdot5$, and $E_0 - E_i = 34\cdot4$.)

Another reference to any former record which includes comparisons with cells whose difference from the chosen reference mean is known, at once fixes the position of the graph; because the difference on the log paper (after using τ) between any two batches has been shown to remain constant. In obtaining the corrections for Table X, curve (1) in fig. 2 will serve as an illustration, and assuming that τ has been found as explained, it is apparent that a knowledge of a single verified comparison with curve (2) or any other known reading, would fix its position. The graph can now be used to read off the corrections, or the equation may be used instead. Using graph (1) in fig. 2 as the supposed graph, it will be seen that the readings must be adjusted to make the mean of the batch + 21 at two months old, — 8 at 16 months, and — 34 at 62 months, it being remembered to use $\tau = 0\cdot75$.

It can now be tried and found that the (P) (Q) graph must lie 15 microvolts above that for the batch, if its value of τ is equal to $20\cdot0$; and that of (Y) (Z) must lie 10 microvolts above that of the batch, if its value of τ is equal to $0\cdot25$. It is, however, clear that with only two or three cells the possible error would be increased by several microvolts, if the calculation were based on them alone.

In addition to the problem of recapturing a given reference value the question arises as to the choice of the best permanent reference mean. The one chosen at McGill University, and used in this paper, was based on the mean value of certain cells with relatively slow preliminary ageing (*i.e.*, with high values of τ), which appeared to remain constant for many months in 1909. These cells were found by exchanges (see Table IV) to be in very close agreement with the means assumed in Teddington and in Washington at that time. It corresponds to the value of the mean of our best thirty neutral cells (having low values of τ), at the age of five months. It is recommended that the value of the e.m.f. of standard acid cells one year old should be taken as the international mean. This would be 66 microvolts lower than the one we have used.

Although one or two batches, of ten cells each, are adequate for recapturing a given reference mean, if advantage is taken of the results of this investigation, it requires many batches to verify the whole procedure and in particular to determine B with accuracy. For a fundamental and independent repetition, it is recommended that the use of ten batches of ten cells each would lead possibly to still greater accuracy, and certainly to a great saving of the labour which was necessary in our case where many indirect comparisons and corrections were necessary to compensate for the gaps and shortages in our readings and in the number of our cells.

In order to illustrate the difficulties that may be encountered through secondary fluctuations and degeneracy of cells, a table of corrected single readings for a large proportion of our old cells is submitted in Table XI.

TABLE XI.—Sample Readings of Cells, Illustrating Variety in Ageing, and Fluctuations in Single Readings.*

Age in Months.	1.	6.	20.	40.	60.	115.	230.	240. (1)	240. (2)
Cell IV	+ 0	+ 0	— 28	— 48	— 55	— 57	— 52	— 52	— 55
„ VI	+ 34	+ 31	+ 20	+ 5	— 4	— 11	— 28	— 15	— 79
„ VIII	— 51	— 61	— 62	— 60	— 60	— 59	— 59	— 61	— 60
„ A	+ 1	+ 1	— 5	— 19	— 21	— 25	— 31	— 31	— 31
„ B	+ 4	+ 0	— 4	— 13	— 17	— 90	— 120	— 120	— 119
„ C 2	— 17	— 14	— 21	— 21	— 23	— 27	— 16	— 16	— 16
„ C 3	— 47	— 15	— 21	— 21	— 30	— 42	— 59	—	—
„ C 5	+ 92	+ 56	— 24	— 49	— 56	— 76	— 98	— 98	— 98
„ D	+ 50	+ 5	— 36	— 62	— 67	—	—	—	—
„ N	+ 36	+ 3	— 19	— 28	— 33	— 51	— 46	— 54	— 45
„ O	+ 37	+ 0	— 21	— 28	— 34	— 51	—	—	—
„ P 1	— 8	— 27	— 38	— 40	— 47	— 57	—	—	—
„ P 2	— 10	— 28	— 29	— 36	— 37	— 39	—	—	—
„ P 3	+ 77	+ 24	— 58	— 92	— 92	— 96	—	—	—
„ P 4	+ 20	— 5	— 29	— 40	— 45	— 96	—	— 234	— 230
„ P 5	— 7	— 30	— 47	— 59	— 59	— 77	—	—	—
„ Q 2	+ 28	— 21	— 53	— 61	— 61	— 62	—	—	—
„ Q 3	+ 6	— 40	— 59	— 55	— 53	— 53	— 69	— 70	— 69
„ Q 4	+ 8	— 2	— 42	— 47	— 57	— 85	—	—	—
„ Q 5	+ 14	+ 3	— 10	— 34	— 49	— 72	—	—	—
„ Q 6	+ 3	— 40	— 48	— 85	— 93	— 108	— 179	—	—
„ 60	+ 30	+ 10	— 31	— 43	— 74	—	—	—	—
„ 63	+ 33	+ 10	+ 3	— 13	— 29	—	—	—	—
„ 64	+ 33	+ 20	+ 3	+ 8	+ 7	—	—	—	—
„ 66	+ 33	+ 8	— 10	— 24	— 35	—	—	—	—
„ 67	+ 30	+ 1	— 3	— 14	— 14	—	—	—	—
„ 68	+ 100	+ 12	— 15	— 28	— 37	—	—	—	—
„ 69	+ 97	+ 47	+ 22	— 3	— 14	—	—	—	—
„ 71	+ 58	+ 6	— 26	— 21	— 40	—	—	—	—
„ 78	+ 3	+ 2	— 14	— 24	— 25	—	—	—	—
„ 79	+ 12	— 24	— 28	— 31	— 36	—	—	—	—
Mean of nine acid cells at above ages	— 66	— 65	— 67	— 67	— 69	—	—	—	—

The Derivation, by the above Methods, of the Ageing Corrections Given in the Tables of Appendix A.

Experience has shown that detailed illustrations are necessary in order to convey clearly the instructions for the technique of this cell accountancy; in conclusion, therefore, the derivation of the ageing corrections which appear at the foot of the tables in Appendix A, are outlined below.

* In other tables, the means of several readings on adjacent dates are used, in order to eliminate secondary fluctuations.

In Table V, the procedure was simple, because the reference batch chosen to give the initial reference mean had not had time to age appreciably, and indeed included some of the cells in this table. The difference between the mean of this batch and that of the one which gives curve (1) in fig. 2 was found from the records for this date to be 10 microvolts, the cells of Table V being the lower.* Now this comparison is referred to the observed point given in fig. 2 at 6·75, which will be seen to be approximately 3 microvolts higher than the graph determined by the analysis of the whole history of that batch; it is thus apparent that the recorded mean for the batch giving curve (1) must be reduced by 3 microvolts to fit the curve, or, as seen in the figure, by 8 microvolts (instead of 5) to give the initial reference mean. Hence the readings of Table V referred to the mean of the batch, must be corrected by $8 - 10 = -2$ microvolts in order to refer them to the initial reference mean. An analysis by comparison with other batches gave the same correction of -2 microvolts in each case. Furthermore, for future use, it could be assumed that the graph for the cells of Table V, if plotted in fig. 2, would lie $5 - (-2) = 7$ microvolts below curve (1) throughout, that is, if none of the cells had to be rejected according to our rules, at some later date.

In Table VI, the correction of -5 microvolts is obtained in a similar manner and need not be described in detail. The comparisons with the cells giving curve (1) were available, and reference to fig. 2, and a knowledge of the ages of the cells involved, lead as before to the given correction. It is thought that there is a possible error of not more than 1 or 2 microvolts for the average of the batch; in the case of a single reading for a single cell, the possible error in the correction would not often be greater than 5 microvolts, largely due to the magnitude of secondary fluctuations, produced by temperature uncertainty or usage of the cell.

In Table VII, a very instructive illustration appears; the cells are approximately 8 months old, and comparisons are available at numerous dates with the cells of curve (1) in fig. 2, *but only when the latter are very much older*. Take for example the occasion of the readings given, the cells of curve (1), fig. 2, averaged 180 months old, and can be seen from the graph to be 52 microvolts below the initial reference mean. The mean of the cells of Table VII were found by direct measurement to be 56 microvolts higher than the mean of the older cells at this time. This makes them 4 microvolts higher than the initial or permanent reference mean. Hence, in order to refer this batch to the permanent reference mean 4 microvolts must be added for this date. Using the known age of 8 months and finding by analysis of other readings that $\tau = 0{\cdot}75$, the point (8·75, + 4) can be marked and a line parallel to the others drawn, thus giving the e.m.f. of the batch both for the past and for the future. When the ageing graph has been recaptured several times in this way to within 1 or 2 microvolts, independently by the use of different batches, confidence in the whole method of procedure

* The facts that the cells are not all quite the same age and that they vary slightly in their values of τ, can be shown to lead to a negligible error at this age in the case of these cells, provided that the average age and the average value of τ are used.

is strikingly justified. When the writer first attempted to disentangle the web of differences in such cases as this and to trace the ageing, it was expected to find variations of many microvolts between the results of different routes of attack, but in only rare instances do discrepancies exceed 5 microvolts.

In Table VIII the ageing correction, — 28, has been determined in the same manner as that used for Table VII, and another description is unnecessary, but it is, however, instructive to note that data such as that obtained from Table VII is generally available for another important method of approach. Usually the correction can be obtained more quickly with the aid of the ageing equation, and past readings, as follows. In the case of these two tables the cells, Nos. 63, 66, 67, 68 and 71, all appear without " rejection " in both tables.

Cell.	From Table VII (8 mos.) referred to initial reference mean.	From Table VIII (60 mos.) referred to mean of batch.	Values at 60 mos. referred to initial reference mean as explained below.
‡63	+ 7	— 1	— 27
‡66	+ 3	— 6	— 32
‡67	+ 4	+ 15	— 11
‡68	+ 6	— 8	— 34
‡71	+ 4	— 11	— 37
Mean . . .	+ 5	— 2	— 28

Now using the ageing equation, it is apparent that,

$$E_{60} = E_8 - 39{\cdot}4 \log_{10} (60{\cdot}75/8{\cdot}75) \text{ microvolts.}$$
$$= E_8 - 33 \text{ microvolts.}$$
$$= + 5 - 33 = - 28 \text{ microvolts.}$$

This means that the second column above should have 26 subtracted from each reading to make the mean reading — 28, in other words the ageing correction is — 26, which when applied will refer the cells to the initial reference mean. This differs from the first given estimate of — 28 by 2 microvolts, but the limited number of cells and the variation of cell ‡67 might have been expected to produce a greater discrepancy.* The following range of values for the ageing correction in this sample case, obtained by different paths, indicate the accuracy of repetition: — 28, — 28, — 30, — 28, — 26, — 28, — 34.

* If Cell ‡67 had been omitted, a change of 4 microvolts would occur in the mean, and the estimated ageing correction would be — 22, but a determination based on only four cells is not acceptable, and in general one would not be content with five cells, either. They are used here to illustrate the method in order to avoid the otherwise lengthy discussion of larger composite tables compiled with cells of different ages, respectively corrected.

In Table IX the same procedures lead to the results given, with the following range of values, necessarily less accurate on account of the much greater age, and the limited supply of the cells : — 40, — 42, — 42, and less reliable estimates, — 45, — 54, — 43. If one uses the total of available observations and comparisons, including batches of acid cells, the uncertainty can be reduced, even in this case, to within 1 or 2 microvolts.

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TABLE IV. International Comparisons of the "Reference Means" of London and Washington in Terms of the McGill Reference Mean for Weston Standard Cells (1908–1928).

(Demonstrating also the accuracy obtainable in applying the ageing corrections to the cells.)

L = value of the National Physical Laboratory mean for neutral cells.
B = value of the Bureau of Standards mean for neutral cells.
Mc = value of the initial McGill reference mean for neutral cells.
X = value of the temporary McGill mean for a given date, uncorrected for ageing.

All readings are in millionths of a volt.

Bureau of Standards and McGill.

Transportation of Cells	Cell Label.	Observations at Bureau of Standards. Date of Obs.	Obs. (B + b)	Observations at McGill. Date of Obs.	Obs. (X + m)	Mc − X as given by ageing curves (a).	(Mc + m − X) = c.	Approximate ageing corrections for interval between observations (a)	B − Mc = a − c − b + e. As deduced from each cell.	Mean value of B − Mc in microvolts.	Error due to shaking, etc., etc. probably less than
(1) From B. of S. to McGill (July, 1908)	511	July 20–22, 1908	B − 5	Jan. 8 & 9, 1909	X + 4		Mc − 2	3	+ 0		
	LV		B 8		X 4	− 6	Mc − 3	3	− 1	− 1	(± 1)
	VI		B + 26		X + 37		Mc − 31	0	1		
(2) From McGill (April, 1909) to B. of S.	A	April 20 & 28, 1909	B + 1	April 29, 1908	X − 8		Mc − 2	0	3		
	42		B − 12		X 5	− 10	Mc − 15	0	2	− 2	(± 2)
	VI		B − 35		X + 47		Mc − 27	0	− 1		
(1) From B. of S. (April, 1909) to McGill	A	April 26 & 29, 1909	B + 1	May 4 & 6, 1909	X + 10		Mc + 3	0	− 1		
	192		B 12		X 8	10	Mc − 12	0	− 2	− 2	(± 2)
	VI		B + 28		X + 10		Mc − 30	0	+ 3		
(3) From B. of S. (Oct., 1918) to McGill	197	Oct., 1918	B 61	Jan. 26–Feb. 21, 1919	X − 8		Mc 52	0	− 1		
	201		B − 48		X − 11	− 4	Mc − 62	0	+ 8	− 2	(± 4)
(3) From McGill (May, 1919) to B. of S.	197	July 24, 1919	B − 50	May 2, 1919	X + 5		Mc − 49	0	+ 4		
	201		B − 42		X + 8	− 56	Mc − 47	0	− 3	0	(± 1)
(11) From McGill (Dec., 1923) to B. of S.	61	Jan. 5–6, 1925	B + 3	Dec. 18, 1923	X 62		Mc + 3	2	− 5		
	65		B + 7		X 59	+ 60	Mc + 0	2	− 6	− 3	(± 3)
	81		B 82		X − 11		Mc − 76	0	6		
(3) From McGill (Oct., 1925) to B. of S.	62	Nov. 18, 1925	B − 18	Oct. 16–24, 1925	X − 30		Mc 3	− 4	+ 9		
	88		B − 61		X − 5	+ 81	Mc − 88	0	0	− 2	(± 7)
(5) From B. of S. (Oct., 1925) to McGill	197	No record received	?	Feb., 1927	X + 7		Mc − 34	0	0 ?	Compare this read B − 30 in (3) above	
	863		?		X + 35	+ 61	Mc − 26				
	864		?		(Intermediate)						
(1) From B. of S. (Oct., 1928) to McGill	61	Oct. 2, 1928	B − 32	Dec., 1928	X + 33		Mc − 27	0	− 5		
	62		B − 64		X + 3		Mc − 62	0	− 2		
	86		B 68		(Extrapolate)	+ 65		0		− 0	(± 3)
	83		B 64		X + 1		Mc − 69	0	− 0		
	84		B 61		X + 1		Mc − 64	0	+ 6		

National Physical Laboratory and McGill.

Transportation of Cells.	Cell Label.	Observations at the Nat. Phys. Lab. Date of Obs.	Obs. (L + l).	Observations at McGill. Date of Obs.	Obs. (X + m).	Mc − X on given date (Taken from ageing curves) (a)	(Mc + m − X) = c.	Approx. ageing corrections for interval between observations. (a)	L − Mc = a − c − b + e. As deduced from each cell.	Mean value of B − Mc in microvolts.	Error due to shaking, etc., etc. probably less than
(1) From N.P.L. (Jan., 1909) to McGill	817	Jan., 1909	L + 0	Feb. 18 Mar. 9, 1909	X − 3		Mc − 5	2	− 3		
	820		L + 0		X + 3	− 8	Mc − 5	2	− 3	− 3	(± 2)
	821		L − 0		X + 3		Mc 5	2	− 3		
(2) From N.P.L. (April, 1909) to McGill	M10	April, 1909	L − 5	May 21 28, 1909	X − 3		Mc 11	2	− 7		
	M11		L 5		X + 8	+ 11	Mc + 2	2	+ 6	− 2	(± 3)
(4) From McGill (Sept., 1911) to N.P.L.	0	Dec. 22–Jan. 19, 1911–12	L − 27	Sept. 14, 1911	X 9		Mc − 27	− 2	2		
	05		L − 21		X − 11	+ 36	Mc − 25	− 2	6	+ 0	(± 4)
	68		L − 31		X + 17		Mc − 19	2	+ 9		
(7) From N.P.L. (June, 1913) to McGill	1-6	June, 1913	L − 10	July 29 Sept. 5, 1913	X + 32		Mc 8	0	+ 2		
	1-8		L − 10		X 41	+ 40	Mc + 1	0	− 14	− 5	(± 5)
(10) From McGill (Sept., 1923) to N.P.L.	54	Nov. 21 Dec. 9, 1923	L − 68	Sept. 17 20, 1923	X 6		Mc − 65	0	+ 3		
	55		L − 65		X − 5	− 59	Mc − 64	0	+ 6	1	(± 2)
	81		L − 69		X − 10		Mc − 69	0	+ 0		