(3) It is shown, by calculations free from assumption as to dilution laws, that the product of the ions of the saturating salt (the so-called solubility product) decreases in value in the cases mentioned with increase in total concentration.

(4) It is shown that in calculations assuming a dilution law, the formula assumed will determine whether the solubility product shows an apparent increase, an apparent decrease, or an apparent constancy.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS LABORATORY OF HARVARD UNIVERSITY.]

ON THE ABSENCE OF THERMAL HYSTERESIS IN THE COPPER-CONSTANTAN THERMOELEMENT BETWEEN 30° AND 100° C.

BY T. W. RICHARDS AND H. W. RICHTER.

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The internal upheaval caused in solid substances by rise of temperature often produces a slight shifting or thermal hysteresis in the properties of these substances, particularly in substances composed of more than one element in a state of solid solution. The shift of a zero point of a mercury-in-glass thermometer is a typical case in point. Although this particular irregularity has been carefully studied and a correction for it can be suitably applied, nevertheless it is a source of annoyance in the use of this type of thermometer.

During the last ten years W. P. White has developed the use of the highly sensitive copper-constantan multiple thermoelement, and has shown the necessary precautions which must be applied in order to solve the somewhat difficult task of measuring electromotive forces of the order of magnitude of 0.0000001 volt, needful to secure the full advantage of this instrument. It seemed desirable to test whether or not the copper-constantan alloy suffers any marked shift of thermoelectric effect on being subjected to rapid changes of temperature.[1] The following note recounts brief experiments, which show the performance of the thermoelement to be more satisfactory in this particular respect than are most other means of measuring small differences of temperature.

A twelve-junction copper-constantan thermoelement kindly made by Dr. White in 1910 was used for the tests. It embodied many refinements. For the present purpose a duplicate twelve-junction thermoelement to put in opposition with this was not necessary, although such a duplicate is highly desirable in ordinary temperature measurements, as White has pointed out.

The measuring apparatus was a 90 ohm Diesselhorst split-circuit potentiometer made by Otto Wolff. This instrument embodied a fixed resis-

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[1] On p. 140 of White's paper of August, 1910 (*Phys. Rev.*, 31), brief reference is made to tests of this nature, but further elaboration seemed to be desirable.

tance of eighty ohms, only ten ohms being reserved for adjustment by means of the five dials. It was connected in series with a resistance of about 2,000 ohms, over which dropped the potential of the cadmium cell used as a standard. The driving cell, a lead accumulator of large capacity, was connected over a total resistance of more than 4,000 ohms, of which the 2090 above specified formed a part. Under these circumstances the maximum range of the Wolff instrument was about four millivolts.

Before use, the driving cell was discharged to a potential of two volts in order that the steep portion of the discharge-curve might be avoided. The resistance of the circuit was, however, not large enough to secure a constant potential; therefore, it was found necessary to adopt the ingenious device[1] of using for the driving battery two storage cells in series, with a third "floated" on the line to act as a regulator. By the use of this device it was found possible to maintain a satisfactorily constant fall of potential over a resistance of 4,000 ohms for an hour at a time. At the end of this time it was ordinarily necessary to make only a small adjustment of the resistance in series with the floating cell.

The thermoelement was in series with a high sensitivity Leeds and Northrup galvanometer of the d'Arsonval type. This instrument, designed for use with the calorimetric resistance thermometer, had a resistance of only 11 ohms, a fact which would have served to accentuate any irregularities inherent in the measuring apparatus or the thermoelement.

The entire measuring outfit was protected from stray currents by means of an equipotential shield. Parasitic electromotive forces were traced by a particularly effective arrangement of eliminating and reversing switches due to the suggestion of Professor Harvey N. Davis of the Physical Department of Harvard University, to whom we are grateful for valuable help. One of these switches was placed in each main circuit, and by their use it was a simple matter to locate any source of trouble. Usually the parasitic electromotive forces (varying from one to four microvolts) in our apparatus came from the galvanometer, which had massive brass binding posts. The rest of the outfit, thanks to the use of jack-knife switches, soldered connections, and thin sheet-copper contacts, was often almost free from thermoelectric trouble, but under bad weather conditions showed serious leakage.[2] Our reversing switches took the place of the simpler eliminating switch used by White. Either arrangement serves well the purpose of correcting for parasitic effects when they remain constant during an observation, but the latter cannot

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[1] "On Increasing the Constancy of Batteries Giving Currents," W. P. White, *Phys. Rev.*, **23**, 447 (1906).

[2] Similar difficulty was found by White in his early work (*Phys. Rev.*, 31, 693 (1910)).

trace them to their source. Either of these, or some other device for neutralizing thermoelectric complications, is absolutely necessary. We have not yet succeeded in wholly avoiding such complications, and in an earlier trial of the thermoelement in 1911 they were large and very changeable.[1]

The tests of the thermoelement under consideration were conducted as follows: Two constant-temperature baths were prepared—one for each arm of the thermoelement. One of these baths was an enclosed and air-jacketed calorimeter submerged in a thermostat[2] kept at about 28.3°, giving a temperature constant to the limit of sensibility of a Leeds and Northrup calorimeter resistance thermometer (0.0003°); while the other bath consisted of sodium sulfate at its transition temperature (32.384°) also air-jacketed in a thermostat. The salt was reasonably

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[1] Over five years ago, in collaboration with Dr. Barry (THIS JOURNAL, 37, 993 (1915)), a description of work performed (in 1911), I decided that the time had not then come (in 1911) for the use of the thermoelement in our calorimetric work. The reason for the decision (which still seems to me to have been entirely wise under the circumstances) was twofold: First, because of discrepancies in a paper entitled, "The Calibration of Copper-Constantan Thermoelements," by W. P. White, and two collaborators published in the preceding August, and, secondly, because of the unsatisfactory performance of the instrument in our own hands. Subsequent correspondence with Dr. White has shown me that I had expected a higher degree of completeness in their paper than had been intended by the authors, hence my judgment against the thermoelement was unduly severe. Dr. White states that this was only "pioneer work, done under unsatisfactory conditions in 1907. Three years later its was published, very briefly, with no idea that it would be taken as a criterion of thermoelectric performance. As you can readily see, from my more complete explanation," Dr. White continued, "the discrepancies discussed in the paper are demonstrably not chargeable to the thermoelement, which really did surprisingly well under the circumstances; the discrepancies which you detected are mainly chargeable to a misleading statement of mine, but apart from that were non-existent." Our own failure to obtain constant results (of which only very brief mention was made) was doubtless due to the thermoelectric inequalities of our potentiometer. This instrument, the best then immediately available, had shown itself to be accurate enough for the electrochemical work for which it had been designed, but it doubtless failed to fulfil the special requirements which Dr. White has shown to be necessary (THIS JOURNAL, 36, 2292 (1914)). It is one thing to attain the accuracy of 0.00001 volt, usually needed in electrochemical work, and quite another to attain the fifty-fold greater absolute accuracy needed for the thermoelement. This latter requirement demands an entirely different technique, as well as instruments of great precision and provisions against certain disturbances, which were lacking in our preliminary work. Hence neither Dr. White's early paper nor our own early experience should be taken as a criterion of the performance of the thermoelement under the best conditions; his later work gives a much clearer idea of its possibilities, as was suggested in the paragraph alluded to at the beginning of this footnote. [T. W. R.]

[2] Essentially this form of bath for comparing thermometers has been in use at Harvard ever since the beginning of adiabatic calorimetry (*Proc. Am. Acad.*, 41, 1 (1905)).

pure, having been four times recrystallized, and the constancy of its transition temperature was at least within 0.001°.

The copper-constantan multiple thermoelement was placed in these baths and allowed to remain for some minutes, during which time its electromotive force was measured and found to be very constant. It was then removed, and one arm was placed in boiling water. During this operation the paraffin insulation was, of course, completely melted. At the end of five minutes the instrument was allowed to cool and replaced in the baths. Preliminary experiments showed the change, if any, to be very small. In the final, most carefully conducted trial, there was no perceptible alteration from the original electromotive force. The value found was 1.8988 (±0.0001) millivolts before and after the treatment, the resistance of the platinum coil in the cooler thermostat remaining exactly at 28.10795 (±0.00003) ohms throughout the trial. In this connection it is interesting to note that the radiation of the electric light bulb which heated the thermostat surrounding the sodium sulfate was enough to affect by its radiant energy that arm of the thermoelement by an amount corresponding to about °0.002. The fluctuation of the electromotive force from 1.8996 with the filament incandescent to 1.8988 with the lighting-current interrupted was clearly marked, and repeated again and again. The values given above are those obtained when the reading was not affected by radiation. This final experiment was performed under very favorable weather conditions, and no leakage was noticed.

Evidently the copper-constantan thermoelement showed in these experiments a highly satisfactory absence of thermal hysteresis. Even after changing the temperature over seventy degrees back and forth within ten minutes, the thermoelectric effect was unchanged within the limit of accuracy of the measurement. This is entirely in accord with the similar but less detailed experience of White already mentioned.

It may seem, perhaps, unwarranted to draw important conclusions from so few observations; and of course it is true that this particularly satisfactory performance of the copper-constantan thermoelement could not alone serve as a criterion of the fitness of this thermoelement for thermometric work. Nevertheless, the property of possessing no thermal hysteresis within these limits of temperature is a qualification so important for accurate thermometry, and so decisive as to the usefulness of the instrument for calorimetric work of high precision, as to recommend it highly to the investigator. The outcome, therefore, inclines us to agree with Dr. White (who has done more than any one else to enhance the usefulness of this form of thermopile) in believing that for those who have an appropriate potentiometer, a sensitive galvanometer and properly constructed copper-constantan thermoelement with two simple but essential accessories, the eliminating switch and equipotential shield, (all used, of course, by a person of adequate experience in electrical measurement of great accuracy), the instrument should be one of great usefulness for comparing small differences of temperature, as in careful work on calorimetry. Dr. White's own papers, especially those of 1914, show that the proper installation of the apparatus is not (at least for the average chemist) an altogether easy task—a conclusion which is not altered by our own experience. Of course the reference to the readings of the instruments to the International Temperature Scale depends upon accurate calibration; and we hope that a new investigation upon this question may soon be published by the Bureau of Standards.

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THE MEASUREMENT OF ELECTROLYTIC CONDUCTIVITY. II. THE TELEPHONE RECEIVER AS AN INDICATING INSTRUMENT FOR USE WITH THE ALTERNATING CURRENT BRIDGE.[1]

BY EDWARD W. WASHBURN AND KARR PARKER.

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1. The Suitability of the Telephone Receiver as an Indicating Instrument for Use with the Alternating Current Bridge.—For determining the bridge setting in an alternating current bridge containing an electrolytic cell, a number of indicating instruments have been proposed and used at different times.[2]

The principal factors which should govern the choice of an indicating instrument for the above purpose are, in the order of their relative importance, (1) sensitivity, (2) ease and convenience in use, and (3) cost.

Now the investigations which have been carried out in this laboratory have demonstrated that a properly constructed telephone receiver is *in every one of the above respects* greatly superior to any of the other instru-

[1] The nomenclature employed in this paper has been given in the preceding paper, THIS JOURNAL, 38, 2431 (1916). The following CORRECTION should be made in the preceding paper: p. 2439, line 23, for "Equations 19 and 20" read "Equations 21 and 22."

[2] Descriptions and discussions of the various types of instruments can be found in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," page 30, and on page 6 of Catalog 48 of the Leeds & Northrup Company, and in the references there cited.