The above method is particularly applicable to electrolytes of any kind if they are placed in a long tube of low heat-conducting material, and the rise of temperature thus measured at a point remote from the electrodes. Then, whatever action, chemical or thermal, occurs at the electrodes, and whatever potential drop may occur, it is only necessary that the amount of current passing be accurately measured, the specific heat and specific gravity of the electrolyte be known, and the rate of rise of temperature be measured at the first few seconds after turning on the current, to be able to calculate the specific resistance.

The use of alternating current for measurements of ohmic resistance using Kohlrausch's method of Wheatstone bridge and a telephone is applicable with accuracy to nonelectrolytic conductors, and has generally been assumed to be applicable quite as accurately to electrolytes. Recent work on the possibility of electrolysis occurring when alternating current is passed through an electrolyte has rather cast doubts upon the accuracy of these tests. It is possible that most determinations thus made have been free from error, but we can understand now that tests so made might be erroneous in many instances, if made with certain electrodes and with. certain frequency of alternation of the measuring current

For many practical purposes, the ohmic resistance of an electrolytic cell can be determined by the following simple device and calculation: Use electrodes equal to the cross section of the electrolyte, and put in series with a relatively high resistance, so as to keep the strength of current as nearly constant as possible. Measure amperes and voltage drop with the plates as wide apart as possible; draw together till they are exactly half the distance apart, and measure again. If the outside resistance is high enough, the amperes will be constant within the ability of the ammeter to record, while the voltage will decrease. Double the decrease in voltage will be the total voltage drop in overcoming the ohmic resistance of the whole cell. Designating this as the voltage drop due to electrical conductivity of the electrolyte, Vc, we have:—

Resistance of cell (in ohms) = -

amperes passing

Vc

Voltage Drop at the Electrode Surfaces.

This is the loss of potential across the electrodes corresponding to the work done at the electrodes. It is practically determinable by measuring the total potential drop, and subtracting from it the drop due to overcoming the ohmic resistance of the electrolyte. Calling V the total drop of potential and V^d that part of it absorbed in chemical (or physical) work at the surface of the electrodes, then

 $V^d = V - V^c$.

If V^c has been determined in the manner described in the last paragraph, or has been calculated from the specific resistance of the electrolyte, properly determined, and the resistance capacity of the electrolytic vessel, then Vd represents accurately the voltage drop due to all phenomena occurring at the surface of the electrodes, as distinguished from the mere phenomenon of electric conduction, ruled absolutely by Ohm's law, occurring in the body of the electrolyte.

It may not be amiss to remark, en passant, that the fact that Ohm's law applies absolutely to the conduction of electricity through the body of an electrolyte, in the same manner as in a metallic conductor, combined with Prof. Hopkins' recent determinations that the conducting of the current is practically instantaneous in electrolytes, as it is in solids, and that the body of an electrolytic conductor acts in all respects magnetically, etc., exactly the same as the body of a metallic conductor—all prove the identity of the mechanism of electrolytic conductor and through solid metallic conductors. The phenomena at the bounding surfaces, the electrodes, are different in the two cases, but there is no experimental evidence of any dissimilarity in [JUNE, 1906.]

the mechanism of the conduction in the body of the conductors in the two cases.

Transier Resistance.

This is supposed to represent resistance to the passage of the current from the electrolyte to the electrode, of the nature of the work done when current is passed across a thermo-electric junction; that is, it is a resistance purely physical in its nature, existing simply because the current passes from one conducting substance to another one, and, finally, a resistance which causes the current to either generate heat, by heating this junction, or to absorb heat, by cooling the junction. It is, therefore, a reversible phenomnon, either subtracting potential from the current in such quantity as that the heat thus generated represents the heat equivalent of the watts thus lost, or else contributing potential to the circuit in such quantity that the potential thus furnished represents, when multiplied by the amperes flowing, the watt equivalent of the heat energy absorbed.

In your lecturer's opinion, this transfer resistance must be very small. Since it would be of different signs at the two electrodes, absorbing voltage at one and generating nearly an equal amount at the other, the difference between two quantities in themselves small, must be of a low order of magnitude. Further, no reliable determinations are at hand concerning these + and - thermo-electrical potentials, because of the inevitable complication of the measurements by purely chemical changes. For instance, one investigator kept two zinc electrodes in zinc-chloride solution, but at 20° C. difference of temperature, and measured the d.fference of voltage, calling it thermo-electric difference of potential; but aside from the fact that this ignores any thermo-electric difference of potential between the hot and cold solutions, or in any part of the external circuit, it is certain that it ignores the difference between the heat of formation of zinc chloride in aqueous solution at two temperatures 20° apart, which might easily be equal to the whole potential difference noted. Until, therefore, physicists have cleared up satisfactorily this whole subject of thermoelectric potential between electrodes and solutions, we are making a less error in leaving out its consideration than in trying to account and allow for it-particularly since we know that some of the so-called allowances are certainly erroneous.

I have left out of the definition of transfer resistance that produced by a change in the electrode whereby a film of insoluble salt or gas is produced, and so chokes off the current. Such action is polarization, and such change in the original conditions, practically introducing modified or even new electrode surfaces, is not transfer resistance, properly speaking.

Voltage Required for Chemical Work.

We arrive here at the kernal of electrolytic calculation, the sole and sufficient basis being that the amount of electrical energy expended in doing chemical work must equal the energy equivalent of the chemical work done. If that position does not lold in this question, then energy could be created or lost, and the principle of the conservation of energy violated. We must admit, however, that if an electrolytic cell cools off while the current is passing, that external heat energy is being supplied which will diminish, by the amount so supplied, the work being done by the current. However, that quantity is in the nature of a possible correction, while the heat of the chemical reaction produced is the principal factor.

We must remark at the outset that the chemical work done means the whole change from the system before electrolysis to the system after electrolysis. There is no division of the chemical work of the current into that required for assumed primary reactions and that for assumed secondary reactions. Only changes taking place at the surface of the electrodes, however, affect the energy requirements; chemical reactions taking place away from immediate contact with the surface of the electrodes neither absorb energy from the circuit nor deliver energy to it—they are purely incidental and independent chemical phenomena.

(Continued.)