The Leakage Method and the Sandwich Type Zisman Method for Measurements of Contact Potential Differences between two Metals Immersed in Poorly Conductive Dielectric Liquids

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The first measurement of contact potentials for metals immersed in a dielectric liquid was reported by H. J. Plumley[1], using a modified Kelvin method, in connection with the problem of the origin of the electrical conductivity of non-polar dielectric liquids. Since then no report has appeared on this subject except those by J. T. Davies[2] who measured the contact potentials at the oil-water interface by applying the Zisman method. Still there remain some important problems to be solved in their measurements. Quite independently of them our efforts have been devoted for several years to extend the Zisman's vibrating electrode method[3] to liquid phase; our intention has been to apply the measurement of contact potential difference (abbreviated to C.P.D.) or surface potential difference as a powerful tool to the research of surface chemical phenomena occurring at metal surfaces immersed in dielectric liquids. The reports on the technique of the measurement[4] and on the distinction between "true C. P. D." and "apparent C. P. D."[5-7] were published previously. The measured values of the C. P. D. between platinum and silver in various dielectric liquids were also reported[8].

Although various methods were reported for the measurement of C. P. D. in vacuo and in gaseous media, the Zisman method has been most widely used because of its convenience especially in gas phase. At an early stage of this research "immersion type Zisman method" was used for the purpose of measuring the C. P. D. between two metals immersed in a dielectric liquid. During the course of this study, it was found that the decrease in the C. P. D. was often caused by the passage of leakage current in the case of conductive dielectric liquids. Therefore, at the present time "sandwich type Zisman method" is recommended as the most suitable one in poorly conductive dielectric liquids. The immersion type Zisman method should be applied only in the dielectric liquids having a very high leakage resistance such as benzene.

The Zisman method, however, is accompanied by a disadvantage, which is that we have to compel one of the two electrodes to vibrate. Vibration of the electrode often brings about troublesome problems in the construction of the apparatus in vacuo or in dielectric liquids. In our laboratory, another new method without electrode vibration for measuring the C. P. D. in dielectric liquids having electrical conductivity was established by employing an electrometer and was named "leakage method". In order to measure C. P. D. without vibrating the electrode, generally, the medium between the two electrodes must have a certain degree of electrical conductivity. In this new method, a small conductivity which is inherent in the liquid was utilized without any additional ionization. Provided that the charge carriers of leakage current do not obey Faraday's laws of electrolysis, the C. P. D. in the liquid can be measured easily by this new method which resembles, in its operation, the ionization method. The ionization method in gas phase has been well known, and that in liquid phase for measuring the interfacial potentials of oil-water was already described by J. T. Davies[9]. But this leakage method utilizing the small electrical conductivity in herent in the liquid is not only entirely new but also interesting. By the analysis of the

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[1] H. J. Plumley, *Phys. Rev.*, **52**, 140 (1937).
[2] J. T. Davies, *Nature*, **167**, 193 (1951); J. T. Davies, *Z. Elektrochem.*, **55**, 559 (1951).
[3] W. A. Zisman, *Rev. Sci. Instr.*, **3**, 367 (1932).
[4] A. Kanamori, *Bull. Nagoya Inst. Tech.*, **6**, 261 (1954).
[5] Y. Yashiro and A. Kanamori, *J. Appl. Phys., Japan*, **23**, 129 (1954); Y. Yashiro, *Bull. Nagoya Inst. Tech.*, **6**, 281 (1954).
[6] Y. Yashiro, ibid. **50th** Anniversary, 343 (1955).
[7] A. Tanaka, ibid., **8**, 293 (1956).
[8] Y. Yashiro, *J. Appl. Phys., Japan*, **24**, 144 (1955).
[9] J. T. Davies, *Trans. Faraday Soc.*, **49**, 683 (1953)

experimental conditions of the two measurement methods, it became clear that, in order to compare directly the values of the C. P. D. obtained by this leakage method with those by the Zisman's, electrical resistance of the liquid between the two electrodes must be approximately 10^7—$10^{12}\ \Omega$. Some of the experimental evidences were also described.

Principles of the Measurement

For the first place, a case of the leakage method is illustrated. A liquid having suitable value of leakage resistance is sandwiched between the metal electrodes A and B as seen in Fig. 1. Under the condition that there exists a C. P. D. between the electrodes, leakage current *i* will flow through the liquid owing to the electrical field arising from the C. P. D. It is desirable that this current flow through the liquid is kept as small as possible throughout the measurement, because there is a possibility that so much of leakage current flow may cause the change in the C. P. D. In Fig. 1, as an excellent null indicator, a dynamic condenser electrometer is employed together with a cathode ray oscilloscope. The C_c is a coupling condenser whose insulation resistance is infinite. Assuming that each of the two electrodes is in a uniform surface state, the dynamic condenser of the electrometer C_e will be charged up by the C. P. D. until the voltage between the points E and F, V_{EF}, just balances the C. P. D. as shown in the round brackets. Then there is no potential difference between A and B, and no current flows*.

For the purpose of measuring this voltage, V_{EF}, this d. c. voltage is converted into an a. c. signal by means of the vibration of C_e, then this a. c. signal is amplified and finally connected to an indicator, e. g. a cathode ray oscilloscope. Under the condition that the voltage between the points E and F, V_{EF}, caused by the C. P. D. is just compensated through the liquid and the input resistor R_i with the aid of the potentiometer P. M. as shown in the square brackets, the input signal to the amplifier must become zero and so the oscilloscope exhibits no signal. Consequently we can determine the C. P. D. between the electrodes A and B from the difference of the potentiometer readings obtained by the change-over of the switch S_1 as in the usual case. The C. P. D. has the same magnitude as the difference of the potentiometer, but with the opposite sign.

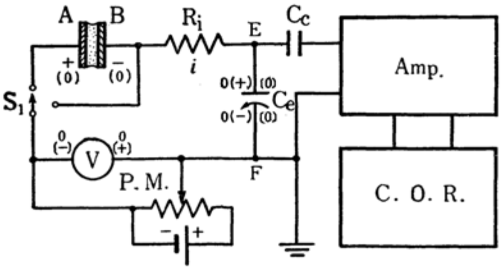

Fig. 1. Schematic diagram of the leakage method.
A, B=the metal electrodes. R_i=input resistor. *i*=leakage current. C_c=coupling condenser. C_e=dynamic condenser of the electrometer. S_1=switch. V=voltmeter. P. M.=potentiometer. Amp.=amplifier. C. O. R.=cathode ray oscilloscope.

At this stage of explanation, we call our attention to the fact that, if we suppose that these two electrodes A and B are the electrodes of an ordinary chemical cell, A is the cathode and B is the anode in the present instance (Fig. 1). On the other hand, when we consider that this voltage is exclusively caused by the C. P. D. between A and B, A is positive with respect to B. However, at the present stage of this research the distinction between electrochemical electromotive forces⁽¹⁰⁾ and C. P. D. which is supposed by the author, is not yet well known in these fields and will become clearer with the progress of this research.

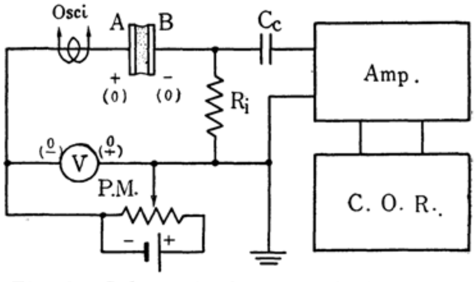

Fig. 2. Schematic diagram of the sandwich type Zisman method.

For the second place, in order to measure the C. P. D. by applying the Zisman method, we connect the circuit as shown in Fig. 2. When one of the two electrodes, A or B,

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* The condition of surface uniformity will be important to measure accurately the C. P. D. or the surface potential difference by the ionization method. Otherwise, errors will probably be introduced.

10) A. Gemant, *Trans. Electrochem. Soc.*, **78**, 49 (1940); A. von Hippel, "Dielectric Materials and Applications", The Technology Press of M. I. T. and John Wiley & Sons, Inc., New York (1954), p. 165.

is vibrated by means of an audio frequency oscillator, an a. c. signal will be generated across input resistor R_i and amplified as in the ordinary case. Under the condition that the C. P. D. is just compensated by the potentiometer as shown in the parentheses, the input to the amplifier will vanish. The C. P. D. must be equal to the reading of the potentiometer, but with the opposite sign in this case again.

Moreover, when the surface state of each electrode is uniform, when the liquid is held between the electrodes A and B like a sandwich, and when the C. P. D. is cancelled by adjusting the voltage of the potentiometer, then the potential difference between the electrodes A and B will disappear and no leakage current flows even though the liquid has electrical conductivity. As shown in our experiments[5], in which the apparent C. P. D. is distinguished from the true C. P. D., the spurious increase in the C. P. D. will not arise in this case. Therefore, the measured values of the C. P. D. using this sandwich type Zisman method must be equal to the true C. P. D. This conclusion was also confirmed experimentally even in nitrobenzene with such a small leakage resistance as that of the order $10^7 \Omega$*. But, in this sandwich type Zisman method too, it is advisable to check this fact occasionally following the method reported previously[5].

Electrical Equipment and Apparatus

In this experiment to check directly the data of C. P. D. measured by this leakage method compared with those obtained by the sandwich type Zisman method, the electrical circuit was connected as seen in Fig. 3. With slight improvements, a dynamic condenser pH-meter (electrometer) was employed as the parts of dynamic condenser C_e and amplifier. A cathode ray oscilloscope was employed as an indicator and the potentiometer was the same as reported previously[6,11]. The operation to measure C. P. D. was illustrated above. Careful attention should always be paid to the shielding of the input circuit to amplifier. All the measurement was carried out by manual null method and the sensitivity of this equipment was within ±2 mV.

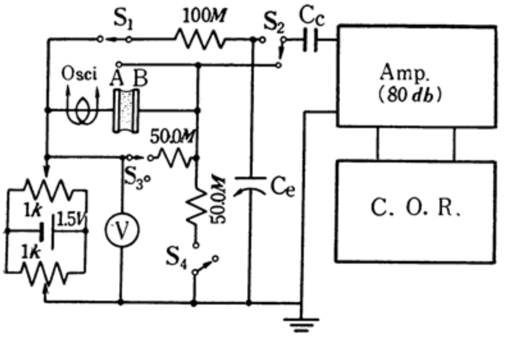

Fig. 3. Practical circuit used in the measurements.
S_1 = switch, same as in Fig. 1. S_2, S_3 = linked switch for the change-over of circuit from the sandwich type Zisman method to the leakage method, and vice versa. S_4 = switch for measuring the true and the apparent C. P. D. Osci. = CR oscillator, operated at 150—160 c/s. C_c = 500 pF polystyrene condenser.

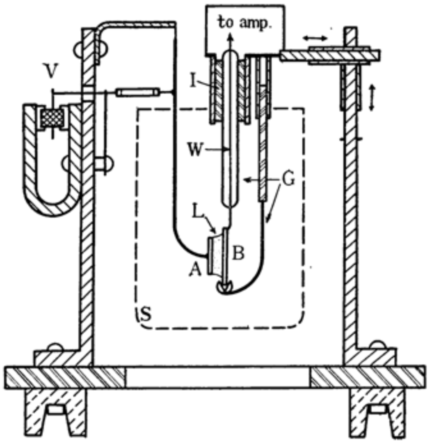

Fig. 4. Apparatus for mounting the electrodes.
V = vibrating reed of magnetic speaker. I = insulator. W = lead wire. G = glass supporter. A = Pt reference electrode. B = sample of metal. L = dielectric liquid. S = shielding.

The part of the electrodes was sketched in Fig. 4, which was designed for another experiment[4] and was used in this measurement too. A dielectric liquid was sandwiched between the two electrodes with a syringe. The distance between the electrodes was so small (0.5—1.0 mm) that the liquid neither dropped down nor evaporated within a short time except when the liquid had very high vapor pressure at room temperature.

Examples of the Measurement

Although electrical potential differences at metal-liquid interfaces will result from various origins, yet the electrical potential difference between two metal electrodes immersed in the dielectric liquids which satisfy the following conditions, should be called "contact potential

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* Details of this experiment will be published in near future.

[11] Y. Yashiro, *Kōbunshi*, **5**, 392 (1956).

difference" of the metals in the liquid according to the author's view. These requirements are as follows;—

1) The decomposition voltage of the liquid, if it exists, must be much higher than the C.P.D. between the two metals immersed in the liquid.

2) In case of the presence of electrical conductivity, the charge carriers of leakage current do not cause chemical reactions with the electrodes by its passage through the liquid. Nevertheless, there may be a case that these carriers cause the change in the C. P. D. by the space-charge polarization arising from the selective accumulation of the carriers at metal-liquid interfaces, when the current is flowing through the liquid under the influence of external electrical field; but this is not involved in the present requirement. Therefore, the term "chemical reaction" should be accepted in its narrower sense and the C. P. D., in its broader sense1) in this statement.

In addition, in order to compare the data obtained by the leakage method with those by the sandwich type Zisman method, it is desirable to choose a liquid having a leakage resistance ranging 10^7—$10^{12}\Omega$ as a sample of measurement for the reasons discussed below. In the present measurement, nitrobenzene and *o*-dichlorbenzene were used.

TABLE I

COMPARISONS OF THE DATA OBTAINED BY THE TWO METHODS

Dielectric liquid	Sample of metal	The leakage method	The sandwich type Zisman method
Nitrobenzene	Al	+500 (mV)	+505 (mV)
	Cu	+220	+220
	Ni	+330	+340
o-Dichlorbenzene	Al	+470	+470
	Cu	+120	+130
	Ni	+415	+410

Nitrobenzene and *o*-dichlorobenzene of chemical pure grade were used after two redistillations. The leakage resistance of the former was $10^7\Omega$ and that of the latter was $10^8\Omega$ under the condition of this measurement. All the metals used were of commercial quality and in the form of a plate (2 cm × 2 cm × 0.5 mm). These plates were polished in the air with clean gauze and purified carborundum powder. The polished-up platinum plate was used as a reference electrode. Within some time from the beginning of the measurement, the C. P. D. values settled into a constant value, then both values of the C. P. D. were obtained by the two methods respectively following the operations described above.

In this measurement, individual values of the C. P. D. were not of great concern, but the degree of agreement of the results by the two methods, was important. As seen in Table I, both data agreed well within the error ±10 mV. Usually the error of this extent will be inevitable at the present stage of this experiment. These samples were all positive with respect to the platinum reference and the data were obtained at room temperature.

Discussion on the Limit of Measurement

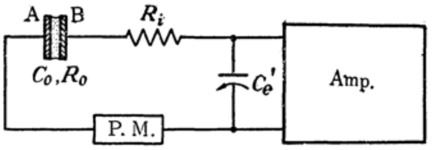

Fig. 5. Equivalent circuit of the leakage method.

C_o = capacitance between A and B. R_o = leakage resistance of the liquid. R_i input resistor, usually 10^8—$10^{10}\Omega$. C_e' = average capacitance of the dynamic condenser plus stray capacitances. Amp. = ideal amplifier, i. e., one whose input impedance is infinite. P. M. = potentiometer, whose internal resistance $R_{P.M.} \ll R_o$ or R_i.

The limit that the C. P. D. can be measured by the leakage method is determined mainly by the magnitude of the time constant of the input circuit. Fig. 5 shows an equivalent circuit of the leakage method, and this belongs to a *CR* circuit. Representing the sum of R_o and R_i by R_s, and that of C_o and C_e' by C_s, the time constant of this *CR* circuit should be $\tau_s = C_s \times R_s$. If this time constant becomes too large, it is practically impossible to measure C. P. D. because too long a time is taken for charging up the dynamic condenser C_e. Considering that the minimum value of C_s experimentally chosen will be, at the best, roughly ten *pF* and that the maximum value of τ_s permitted by practical operations will be several seconds, R_s or R_o should be smaller than the order of $10^{12}\Omega$ where $R_o \gg R_i$. In this method, however, no limitation is required on the lower range of R_o.

In the sandwich type Zisman method (Fig. 2), however, the lower limit does exist but the upper limit does not. As the leakage resistance of the liquid becomes smaller, the a. c. voltage generated by the electrode vibration decreases correspondingly and, at last, becomes comparable to the intrinsic noise of the amplifier; in other words, the lower limit of R_o will be determined mainly by the amplifier sensitivity. Full analysis of this problem is so complicated that it is beyond our scope in this experiment. Perhaps it will be sufficient for the present purpose to determine this lower limit experimentally on the simplest condition. When all the electric circuit constants remain unchanged except R_o, the lower limit of R_o is roughly $10^7 \Omega$ in the equipment shown in Fig. 3.

Therefore, only in the liquid having leakage resistance of 10^7—$10^{12} \Omega$ or specific resistance of 10^8—$10^{13} \Omega \cdot \mathrm{cm}$, can the measured values of the C. P. D. by the leakage method and by the sandwich type Zisman method, be compared with each other.

Summary and Conclusion

For the purpose of measuring the C. P. D. between two metals immersed in poorly conductive dielectric liquids, two methods were presented in this report. One is the leakage method, which appears to resemble the ionization method but is different in one point; because in this leakage method we make use of the small electrical conductivity inherent in the liquid. It is another merit of this method that the measurement can be carried out without vibrating the electrode. When the liquid and the electrodes are properly chosen, this leakage method may be applied to various purposes. The other is the sandwich type Zisman method, which is an excellent device of improvement of the vibrating electrode method in dielectric liquids. On the comparison of the measured values by the two methods, satisfactory agreements were obtained.

Of course, there is only limited knowledge at the present time on the nature of the electrical potentials observed in these dielectric liquids, yet the author ventures to say that the use of the term, "contact potential difference", is most suitable in the case of these experiments.

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