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# A MODIFICATION OF THE IONIZATION METHOD ESPECIALLY SUITABLE FOR CONTINUOUSLY RECORDING CONTACT POTENTIAL DIFFERENCES

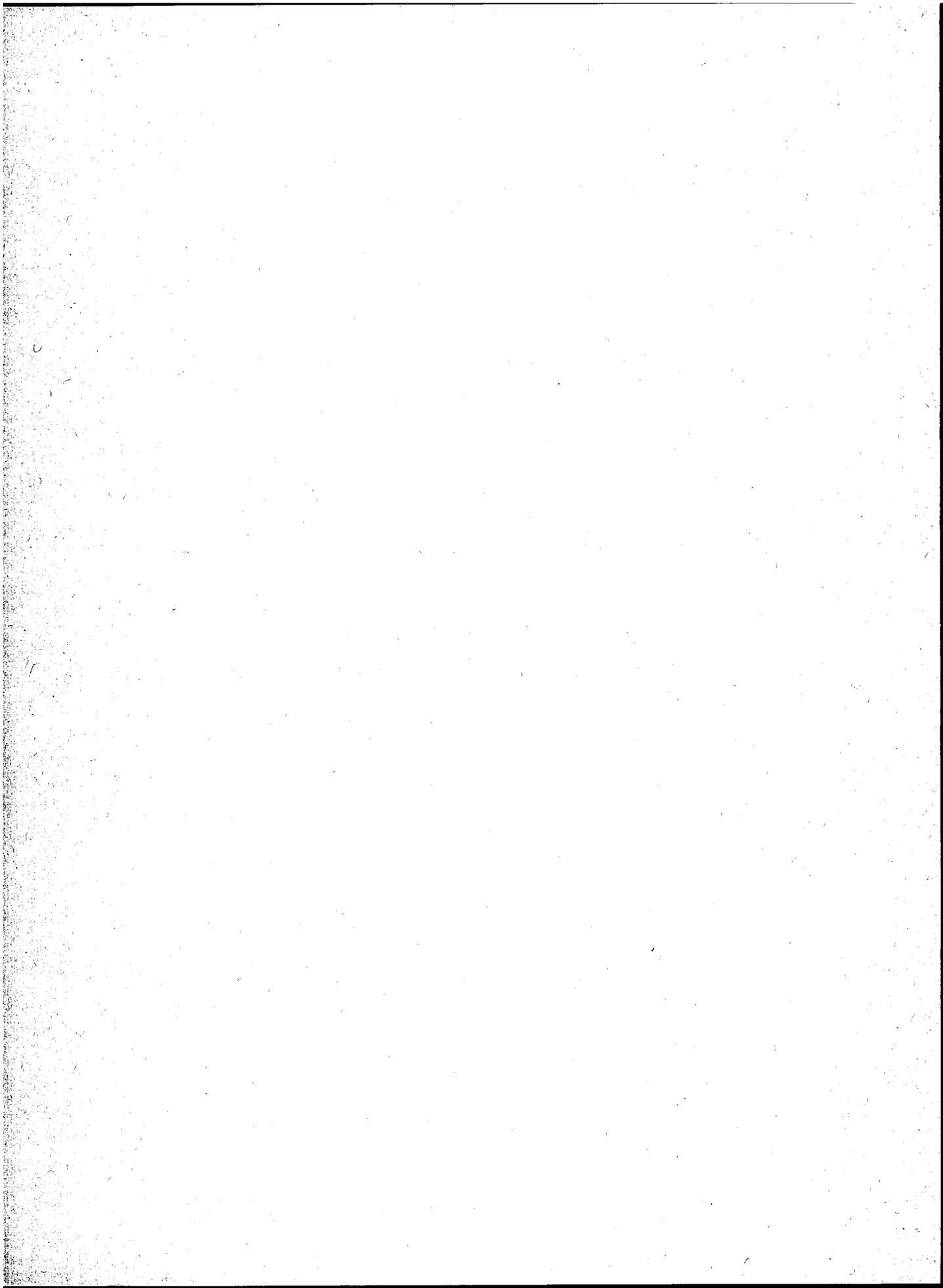
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### ABSTRACT

Ions formed in the air space between two different conducting surfaces will migrate in the electric field and produce a current in an external circuit proportional to the contact potential difference. Since the ionization method of measuring contact potential involves a direct-current output, it is more adaptable for continuous recording than are other methods, such as the vibrating condenser method. A study was made of the factors which minimize the inherent errors of the ionization method and of a modification which permits the use of an ordinary low-impedance-input dc chart-type voltmeter and the use of a wide air spacing desirable for certain applications. The modification is an accounting for errors introduced by a wide spacing between the ionizing source and the surface being studied, the wide spacing causing the air-space impedance to be comparable to the impedance of the indicating meter. In comparing the vibrating condenser method and the ionization method it was determined that in those cases where gaseous adsorption is not a factor the ionization method did show much greater sensitivity as well as permit continuous dc voltmeter recording.

### PROBLEM STATUS

This is an interim report; work on this problem is continuing.

### AUTHORIZATION

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## INTRODUCTION

There are several ways of measuring the differences in the work functions of vacuum outgassed metals, heated filaments, semiconductors, and crystalline solids, or of liquids (1). The vibrating condenser method (2,3), a modification of the Kelvin condenser method (4), is particularly suitable for measuring the difference in contact potentials produced by films of gases and polar and nonpolar organic compounds on liquid and metal surfaces. However, in some situations the ionization method (5,6) has certain distinct advantages, particularly when a continuous recording of the contact potential variation with time is required. A good historical bibliography of this field of research has been compiled by Patai and Pomerantz (7).

This report is concerned with the factors which minimize the inherent errors and influence the accuracy of the ionization method, and with a modification of the method which permits the use of ordinary dc chart-type voltmeters to record directly the time variations in contact potential differences.

## THE IONIZATION METHOD

When two different conducting surfaces are connected together by an ammeter, a condition of charge equilibrium is established in the system and an electrostatic field is produced in the air space between the conductors which gives rise to the contact potential difference between them. As is well known this contact potential difference is equal to the difference in the electronic work functions of the two dissimilar conductors. If ions are formed in the air space, they will migrate under the influence of the electric field strength, and a current proportional to the contact potential difference will flow in the external circuit.

The ionization method is analogous to the Kelvin condenser method (4) and the vibrating condenser method (2,3) in that the factors of geometry of the two conductors, their surface chemical constitution, and the atmospheric state of the air gap all contribute to the magnitude of the current flowing in the circuit. However, there is one important difference: the Kelvin method produces a transient flow of electric charge, and the output of the vibrating condenser method is an alternating current, but the ionization method output is a direct current. This dc current is more easily directly related to a contact potential difference than the transient charge or the ac current output of the first two methods.

Figure 1a shows two opposing conductors, A and B, connected together through an indicating meter, M. One of the conductors, B, is a source which produces ions in the air gap between A and B. This circuit is electrically equivalent to the schematic diagram of Fig. 1b:  $V$  is a dc source whose voltage is equal to the contact potential difference between A and B,  $R$  is the resistance of the ionized air space between A and B, and  $r$  is the resistance of the meter M across which the voltage  $e$  is measured. The problem is to measure  $V$ . Obviously, if  $r \gg R$ , then M can be a dc voltmeter and  $V$  can be determined directly. It will be shown later that  $R$  can be of the order of  $10^{10}$  ohms (8); in such a

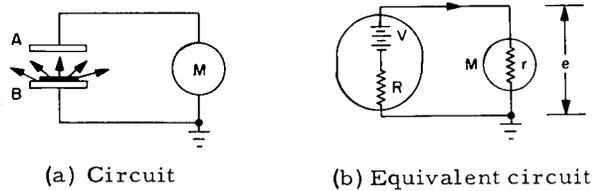


Fig. 1 - The ionization method circuit

case  $M$  must necessarily be an electrometer type meter. If rapid changes in  $v$  are to be observed, the  $rC$  time constant of  $M$  would have to be small enough so that it would respond to these changes; for example, with  $R = 10^{10}$  ohms and an effective input capacitance of 100 picofarads (including the shunting capacitance of the connecting cable to the ionization cell), it would take 3.1 seconds for the meter to reach 95% of the true value of a sudden step function change in the contact potential between  $A$  and  $B$ . A more serious objection is that with long connecting cables it would be difficult to shield the electrometer input against noise.

$v$  can also be measured by using a conventional multirange voltmeter, in which case the condition would be that  $R \geq r$ . This is done by making two measurements of the output voltage,  $e_1$  and  $e_2$ , on two different ranges of the voltmeter,  $M$ , having known input resistances,  $r_1$  and  $r_2$ . The required relations are then obtained as follows:

Since  $e_1 = i_1 r_1$  and  $e_2 = i_2 r_2$ , then

$$V = i_1 R + e_1 = e_1 \left( 1 + \frac{R}{r_1} \right) \quad (1)$$

$$V = i_2 R + e_2 = e_2 \left( 1 + \frac{R}{r_2} \right) \quad (2)$$

$$R = \frac{e_2 - e_1}{\frac{e_1}{r_1} - \frac{e_2}{r_2}} \quad (3)$$

Evidently,  $R$  can be obtained from Eq. (3), and  $V$  can then be calculated by (1) or (2). After one determination of  $R$ ,  $e_1$  or  $e_2$  can be recorded continuously if the reference potential of the ionizing source,  $B$ , remains fixed during the elapsed time. This important qualification will be discussed later.

The usual way  $v$  is determined by the ionization method is to use a null device. If a battery,  $E$ , is placed in series with the two conducting surfaces, as shown in Fig. 2a, and its potential is equal to  $V$  and opposite in polarity, then  $M$  becomes merely a null indicating meter. However, this method is not easily adaptable to continuous recording since this would require a servomechanism to continuously adjust the null battery,  $E$ .

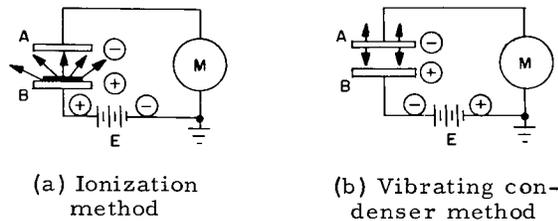


Fig. 2 - The null battery polarity of the vibrating condenser method and the ionization method

## THE IONIZING SOURCE

Either of two alpha particle radiators is generally used as a source of ions:  $\text{Ra}^{226}$ , which has a range of 3.39 cm, or  $\text{Po}^{210}$ , which has a range of 3.92 cm in air at  $15^\circ\text{C}$  and 1 atmosphere pressure (9). Again referring to Fig. 1a, this ionizing range determines the magnitude of the dc current. Greinacher (10) showed that, owing to the short range of the alpha particles, the magnitude of the meter deflection depends upon the separation of A and B. In order to utilize completely the ionizing potentialities of the source, the radiation proceeding from it should traverse a certain optimum thickness of air. Upon increasing the separation of the plates, the effect of recombination of ions enters, causing a subsequent decrease in the current.

Although the contact potential difference between two surfaces is a physical property of those surfaces, the ionization method, if not used properly, can make it appear that it depends on the spacing between them. There is also another factor superimposed on the ionization mechanism which causes an additional apparent change in the contact potential. The ion source, B, of Fig. 1a is a radioactive foil bonded to a thick metal base plate; consequently the radiation pattern is hemidirectional. The ionization that takes place outside of the opposing faces between A and B will vary with the distance between them; furthermore these ions may migrate to the side and back surfaces of A and B, where the contact potentials differ from the prepared opposing faces. This behavior is somewhat analogous to the electrostatic fringing flux which was discussed in the vibrating condenser method (3), except that electrostatic flux lines follow a path of orthogonal curvilinear squares whereas migrating ions diffuse in an electric field.

## THE EXPERIMENTAL STUDY

### The Radioactive Electrode

The radioactive electrode used in these experiments was fabricated by the U.S. Radium Corporation, Morristown, New Jersey. It consisted of a 6-mm-square foil activated with radium-226 sandwiched between a silver base-plate and a gold overlayer. The gold coating on the working face reduced the ionization range of the alpha emission to 1 cm in air at standard conditions. The specified activity of the electrode was 5 microcuries (185,000 disintegrations per second). This active foil was bonded to a larger brass mounting plate  $7/8$  inch in diameter. Electrode A was a circular solid gold disk  $3/8$  inch in diameter.

### The Indicating Meter

The indicating meter used was a Keithley electrometer, type 610A. As an electrometer voltmeter this instrument has an input impedance of  $10^{14}$  ohms resistance shunted by a capacitance of 30 picofarads. It can also be used as a current meter by indicating the voltage drop across shunting resistors whose values vary in decade steps from  $10^{11}$  ohms to 10 ohms.

## Results

In Table 1,  $d$  is the spacing in millimeters between A and B,  $V(\text{dc})$  is the electrometer voltage when  $r = 10^{14}$  ohms,  $V(\text{null})$  is the voltage of a null battery inserted between B and the ground terminal of M,  $r_1$  and  $r_2$  are the two meter resistors across which the measured voltages  $e_1$  and  $e_2$  are obtained,  $R$  is calculated from Eq. (3), and  $V(\text{calc})$  is calculated from Eq. (1).

Table 1  
The Contact Potentials Measured by Three Modifications of the Ionization Method ( $r_1 = 10^{10}$  ohms and  $r_2 = 10^9$  ohms)

d (mm)	V(dc) (volts)	V(null) (volts)	$e_1$ (volts)	$e_2$ (volts)	$R \times 10^{-10}$ (ohms)	V(calc) (volts)
0.3	0.216	0.219	0.135	0.032	0.557	0.211
0.4	0.217	0.221	0.138	0.035	0.486	0.204
0.5	0.219	0.220	0.139	0.037	0.442	0.201
0.6	0.216	0.219	0.138	0.036	0.447	0.199
0.7	0.215	0.220	0.139	0.037	0.442	0.201
0.8	0.220	0.221	0.140	0.038	0.425	0.199
0.9	0.226	0.224	0.140	0.038	0.425	0.199
1.0	0.224	0.228	0.139	0.037	0.442	0.201
1.5	0.223	0.239	0.134	0.034	0.494	0.178
2.0	0.220	0.238	0.121	0.030	0.508	0.182
2.5	0.219	0.239	0.111	0.026	0.521	0.167
3.0	0.214	0.239	0.101	0.025	0.510	0.152
3.5	0.210	0.237	0.096	0.022	0.596	0.153
4.0	0.209	0.237	0.085	0.019	0.628	0.139
5.0	0.201	0.237	0.077	0.019	0.512	0.116
6.0	0.189	0.237	0.071	0.018	0.437	0.102
10.0	0.175	0.236	0.051	0.017	0.286	0.066

The residual noise voltage was measured by replacing the ionizing source with a dummy metal electrode. When  $r = 10^{14}$  ohms,  $V(\text{noise}) = 0.027$  volt. When  $r = 10^{10}$  ohms or  $10^9$  ohms,  $V(\text{noise})$  was less than 0.001 volt. Thus the residual noise was not a contributing factor in the measurements; however, effective electrostatic shielding was provided around the electrodes A and B and the connecting circuitry in order to obtain this low noise contribution.

The data of Table 1 show that, for small values of  $d$ , the electrostatic fringing field between A and B and the extraneous ionization outside of the air gap are both negligible; consequently,  $V(\text{dc})$ ,  $V(\text{null})$ , and  $V(\text{calc})$  are all in close agreement with the true value of the contact potential difference. As  $d$  increased,  $V(\text{dc})$  passed through a maximum value at the optimum ionization range, after which it decreased as recombination and extraneous ionization became important.

$V(\text{null})$  on the other hand is insensitive to any change in the ionization; the null battery serves merely to cancel the electrostatic field produced by the contact potential difference between A and B. Thus  $V(\text{null})$  shows a variation of only 0.020 volt due to the change in the fringing flux for the two electrodes in question. Although this error is the least of the three methods considered, the  $V(\text{null})$  method is not suitable for continuous recording.

$V(\text{calc})$  is subject to the same errors resulting from recombination and extraneous ionization as  $V(\text{dc})$ , but in addition for large values of  $d$ ,  $V(\text{calc})$  is obtained from the difference and division of two small numbers,  $e_1$  and  $e_2$ . As an illustration, from

Table 1 when  $d = 10.0$  millimeters, an error of 1.0 millivolt in  $e_1$  and  $e_2$  will cause an error of 9.1% in  $V$  (calc).

In spite of the indicated objections,  $V$  (calc) is the most reliable method of time recording for some experimental conditions. One such case would be the measurement of contact potentials between a metal electrode and the surface of the water in a Langmuir-Adams film balance. It is extremely difficult to obtain adequate electrostatic shielding of an electrometer with such a large exposed electrode. With the ionizing source placed above a grounded tray of water, any slight movement within several inches of the electric field coupled to the measuring loop of the electrometer caused a change of several hundred millivolts when  $r = 10^{14}$  ohms. When  $r = 10^{10}$  ohms, this electric field disturbance was more than three orders of magnitude less, and readings of  $e_1$  and  $e_2$  could readily be made.

The data in Table 1 show that when  $d = 1.0$  millimeter, the error in  $V$  (calc) is only 0.010 volt less than the value of 0.211 volt obtained when  $d = 0.3$  millimeter. Thus one determination of  $R$  at the larger spacing would allow  $V$  to be determined continuously from a recording of  $e_1$  with an expected error less than 5% resulting from the increased spacing. The spacing,  $d$ , could be increased to 10 millimeters by enlarging the area of the ionizing electrode ten times; this would maintain the same area-to-spacing ratio of A and B with a comparable degree of extraneous ionization.

#### COMPARISON OF THE IONIZATION METHOD WITH VIBRATING CONDENSER METHOD

The sensitivity of the vibrating condenser method, and consequently its reset accuracy, is a function of the ratio of the area of the electrodes to the spacing between them (3). Since this method involves an ac current measurement, the limiting factor of the reset accuracy is the signal-to-noise ratio of the null indicator. With use of a standard null detector (General Radio 1232-A) the practical limit of the reset accuracy was  $\pm 0.001$  volt; with electrodes  $3/8$  inch in diameter, the maximum allowable spacing for this accuracy was 0.5 millimeter. The use of a cathode follower coupling stage between the vibrating condenser and the null indicator has been discussed in Ref. 3; in order to improve the signal-to-noise ratio of the system with this device, extremely careful electrostatic shielding of the cathode follower is necessary.

The sensitivity of the ionization method is independent of the spacing between the electrodes; the accuracy depends upon the reading of the dc output voltmeter itself. If this voltmeter takes the form of a potentiometer bridge, the accuracy can be better than 1 part in  $10^4$ , or  $\pm 0.001$  volt if this value represents the noise fluctuation of the system. Thus the ionization method has a distinct advantage with regard to the maximum working spacing between the electrodes.

The ionization method is useless in some circumstances. Obviously, it cannot be used in high-vacuum systems since no ionization would occur without a collision process. Also it cannot be used in varying gaseous atmospheres since the adsorption and desorption of changing gases and vapors on the gold overlayer of the ionizing electrode would change its reference potential. The vibrating condenser reference electrode can be coated with a thin Teflon film, a low energy surface which does not adsorb many gases and vapors in standard atmospheres (11); this permits the study of gas phase adsorption and desorption with the vibrating condenser method. An ionizing source cannot be coated with Teflon because alpha radiation will not pass through such a thick dielectric film. Also, any ionizing radiation would quickly electrostatically charge the dielectric, thus making it impossible to maintain a fixed reference potential.

It should be pointed out that just as in the case of the ionization method the noise pickup voltage present in the vibrating condenser method is proportional to the input impedance of the indicating meter; the input impedance of null amplifiers used with the vibrating condenser method is of the order of  $10^6$  to  $10^8$  ohms, which is easily low enough to make the method suitable for film balance work where an unshielded reference electrode is used. Hence if sensitivity is the main concern, the ionization method is preferable to the vibrating condenser method, but if gaseous adsorption on the reference electrode is a factor, the vibrating condenser method is preferable.

One important consideration in the study of adsorbed monolayers and films is the effective polarity of the vertical component of the moment of the adsorbed dipole. The use of a null battery in the vibrating condenser method requires that a charge of equal magnitude and opposite sign be placed on the condenser plates in order to nullify the electric field of the contact potential. The polarity of such a battery is shown in Fig. 2b, where the potential of A is negative with respect to B. In the ionization method the source AB is equivalent to a dc battery, and in order to obtain a null for the same relative potential of A and B, the null battery polarity must be reversed as shown in Fig. 2a.

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