

Non-Equilibrium Method for the Direct Determination of Potentials of Zero Charge

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Disturbance of double-layer equilibrium at the electrodes causes transient changes in e.m.f. of a galvanic cell. The change of this effect with the concentration of potential-determining ions can be used to locate the potential of zero electrode charge. This general method is checked for the AgI/water interface.

The electrical behaviour of the "non-polarizable" interface between solids such as AgI and electrolyte solutions is often described under the assumption of permanent equilibrium conditions, i.e., of surface charge and potential difference between solid and solution being completely determined by the composition of the solution. This assumption, however, can only be a crude approximation when it comes to the description of rapid processes like Brownian collision of colloidal particles or the adaptation of the electrical double layer to sudden changes in electrolyte concentration.

Consider an AgI-surface in contact with an electrolyte solution. The surface will be in equilibrium with the I^- ions in the solution and therefore carry an electrical double layer with a charge of a few $\mu C/cm^2$. Addition of a salt solution of different ionic strength will alter the double-layer capacity at the interface. Since double-layer capacities are adjusted in short times (e.g., 10^{-7} sec) it would take high exchange currents ($10 A/cm^2$) to maintain equilibrium.

Exchange currents depend on the concentration of potential-determining ions, and conditions could easily be chosen so that they are in the $\mu A/cm^2$ order of magnitude. Under such circumstances it would take seconds to restore equilibrium after the addition of inert electrolyte.

EXPERIMENTAL

We measured the effect described above in a galvanic cell consisting of the AgI-electrode under consideration and a reference electrode insensitive to changes in ionic strength. The addition of inert electrolyte will cause a transient deviation from the equilibrium cell e.m.f. In order to interpret observed changes as a change in the double-layer potential of the AgI-electrode, one should be able to differentiate between spurious effects upon the activity due to the initial incomplete mixing of salt solutions in the cell and those caused by the slow readjustment of the electrode charge to its equilibrium value.

We were able to do so by adding a solution of inert electrolyte containing so much of the potential-determining KI, as to shift the equilibrium electrode potential in a direction opposite to the shift caused by an increase in double-layer capacity through the addition of inert electrolyte. Fig. 1 is an aid to explain this technique. It represents the adsorption isotherms of potential-determining ions at the AgI/water interface.^{1-3, 5}

By adding, e.g., 1 ml 1 M KNO_3 , $pI = 4$, to 100 ml 10^{-3} M KNO_3 , $pI = 7$, a simultaneous change is brought about in the concentrations of KNO_3 and I^- in our cell. The effect of KNO_3 addition is an increase of double-layer capacity which, at constant surface charge σ ,

makes the AgI-electrode seem more positive. Simultaneously, the added I^- fixes the equilibrium electrode potential at a more negative value, and helps to restore equilibrium along the isotherms. The relative speed of these two processes determines the actual direction of the deflection from the original electrode potential. Incomplete homogenization of the solutions in the cell will not affect the simultaneity of these two tendencies and may even increase both the effects of extra KNO_3 and I^- -concentrations, without changing their respective directions or their relative speed. The time needed to reach final equilibrium depends on the exchange

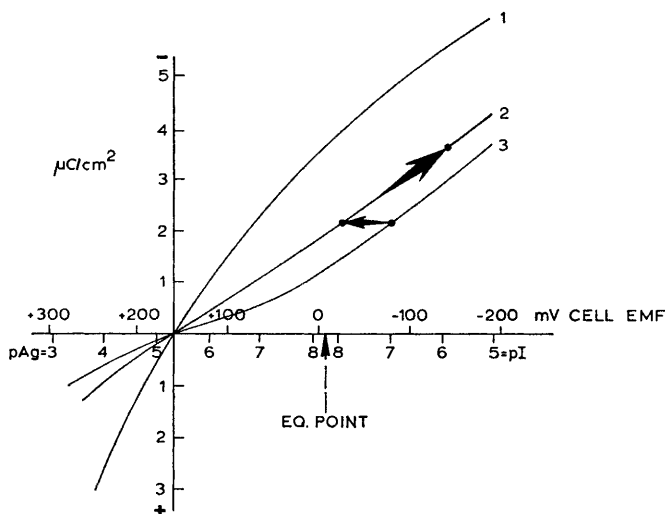


FIG. 1.—Adsorption isotherms of potential-determining ions on AgI for different concentrations of KNO_3 . Isotherm 1, 10^{-1} M KNO_3 ; 2, 10^{-2} M; 3, 10^{-3} M.

current density. It should increase with decreasing concentration of potential-determining Ag^+ and I^- ions. The maximum time will be needed around the equivalence point $pI = pAg = 8$.

The influence of the inert electrolyte should also be dependent on pI . In fig. 1 it is seen to vanish at the potential of zero charge (p.z.c.) near $pAg = 5.4$. The technique described may therefore constitute a quick and general way for direct determination of the p.z.c. of an electrode. We checked this for the AgI/electrolyte interface, where the p.z.c. is relatively well known from electrokinetic⁴ and adsorption¹ measurements.

MATERIALS

Water was distilled from alkaline permanganate and redistilled twice in a three-stage distillation apparatus under a purified nitrogen atmosphere. KNO_3 was recrystallized from triple-distilled water, and heated up to $300^\circ C$ before use. A.R. KI was not further purified, but heated up to $300^\circ C$; $AgNO_3$ A.R. was heated to $200^\circ C$. Nitrogen was dried over silica gel after purification with a B.T.S. catalyst (B.A.S.F.) to remove oxygen. All glassware was cleaned with hot nitric acid and thoroughly steamed afterwards.

ELECTRODES

Three kinds of AgI-electrodes were prepared.

(a) ELECTRODES WITH A SMOOTH AgI SURFACE. Pure silver cylinders (length 50 mm, diam. 5 mm) were polished with Brasso metal polish (Reckitt N. V., de Bilt, The Netherlands) until they showed a smooth and bright appearance. Then they were heated to $300^\circ C$. While still warm they were allowed to react with iodine vapour under reduced pressure (50 mm Hg) for 7 min. The reddish-yellow coloured electrodes were aged in a 10^{-4} M KI solution

at 65°C for 6 h and kept under triply-distilled water overnight before use. During the aging period the colour of the electrodes turned to violet.

The smoothness of these electrodes has the advantage that additional diffusion processes in a spongy structure at the electrode/solution interface are avoided. Similar electrodes, prepared for double-layer capacity measurements, were studied by electron microscopy. They showed a closed surface of sintered microcrystals; the roughness of the AgI-surface is of the order of 1000 Å.

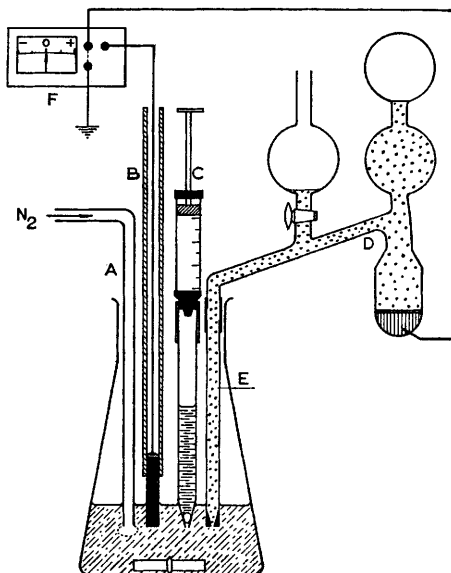


FIG. 2.—Experimental set-up. A, gas inlet tube; B, AgI electrode; C, syringe connected to Pasteur-pipette; D, calomel electrode (10^{-1} M); E, van Laar capillary.

(b) **AgI-ELECTRODES PREPARED BY ELECTROLYSIS.** A smooth Pt-wire was plated with silver by 30 min electrolysis in a $\text{KAg}(\text{CN})_2$ -solution (current density 10 mA/cm^2) and then electrolyzed in a 2 % KI-solution for 15 min at a current density of 2 mA/cm^2 .⁶

(c) **AgI-ELECTRODES PREPARED BY ELECTROPHORETIC DEPOSITION (COLLOID ELECTRODES).** A silvered Pt-wire (see (b)) was covered with particles from a concentrated aged AgI-sol⁷ through electrophoretic deposition at 2 V/cm field strength.⁶

(d) **REFERENCE ELECTRODE.** As a reference electrode a 0.1 N calomel electrode was used.^{4, 8} It was provided with a van Laar^{1, 9} capillary serving as a salt bridge and so had to be under extra pressure.^{3, 5} The resistance of the capillary was $3 \times 10^5 \Omega$. It represented practically the total internal resistance of the galvanic cell.

THE CELL

The galvanic cell is shown in fig. 2. It consisted of a 200 ml Erlenmeyer flask, into which were hung a Pasteur-pipette connected to a 1 ml syringe C with a rubber ring; the AgI-electrode B; the van Laar-capillary of the reference electrode E and a gas inlet tube A. Nitrogen was bubbled through the solution that was stirred with a glass-covered magnetic stirrer. The solution in the Pasteur-pipette was separated from the bulk solution by an air bubble in the narrow tip. Electrical leakage was prevented by mounting the electrodes on separate stands.

VOLTAGE MEASUREMENT

The cell e.m.f. was measured with a John Fluke differential voltmeter type 825 A.R. This is a potentiometer, equipped with a direct reading voltmeter to indicate the unbalance

of the potentiometer device. The sensitivity for direct reading can be chosen in ranges from 2 mV to 10 V full scale. The input resistance per volt of input voltage for 1 % of full-scale off-balance at the ranges used was $10^{11} \Omega$. The instrument has a chopper frequency of 94 c/sec.

PROCEDURE

100 ml of a 10^{-3} M KNO_3 solution were brought into the clean Erlenmeyer flask. A few drops of a 10^{-3} M solution of AgNO_3 or KI were added to give the e.m.f. of the cell a pre-selected value. The solution was vigorously stirred and nitrogen was bubbled through. To check the absence of mechanical or electrical errors before every experiment a blank experiment was run, in which 1 ml was sucked from the solution into pipette C, and re-injected into the flask. The cell e.m.f. was not disturbed by this procedure.

Next, pipette C was filled with 1 ml 1 M KNO_3 containing enough KI or AgNO_3 to change the equilibrium e.m.f. The first experiments were done with a 1 M KNO_3 , 10^{-4} M KI solution, but later the KI concentration was varied so as to give a much smaller shift in pI. Between the equivalence point ($\text{pAg} = 8$) and the p.z.c. ($\text{pAg} \sim 5.4$) it is possible to use 1 M KNO_3 without extra I^- , the decrease in activity coefficients causing a shift in e.m.f. in the desired (negative) direction.

Before the rapid introduction of the 1 ml 1 M KNO_3 the cell e.m.f. was compensated with the John Fluke potentiometer. Changes in the cell e.m.f. appeared on the voltmeter's direct reading dial, 2 mV change giving full scale deflection from zero to either + or - direction. The final equilibrium e.m.f. was measured by the normal compensation procedure.

RESULTS

With this procedure we observed two consecutive deflections from equilibrium e.m.f. The initial quick one—dependent on pAg—is shown in fig. 3. The second one (in the opposite direction) results from the new equilibrium e.m.f. and passes meter balance in the time also indicated in fig. 3. We do not attach importance to the absolute magnitude of either the measured deviations from equilibrium e.m.f. caused by the addition of inert salt, or the time before final equilibrium is reached since they are influenced by incomplete mixing of the solutions.

We nevertheless report some of the observed values in fig. 3 because they show the order of magnitude of both effects and their dependence on pAg. The direction (sign), however, of the transient deviation from equilibrium is important since it enables us to distinguish between the influence of the change in double-layer capacity and that of surface charge.

Apart from the experiments of the type shown in fig. 3 we proved that the positive and negative deflections from equilibrium were caused by KNO_3 and KI respectively. We ran a series of blank experiments in which we added either 1 M KNO_3 without extra I^- at $\text{pI} = 7$, or KI without changing the ionic strength (10^{-3} M KNO_3 $\text{pI} = 4$). In this way the positive and negative deflections were observed separately.

In fig. 3 we see that a small positive deflection from equilibrium is sometimes observed at $E > 165$ mV.* This value is rather insensitive to changes in pAg. We therefore considered it constant and attributed it to other effects, such as diffusion-potential changes. Its 0.3 mV were subtracted from the measured pAg-dependent deflection caused by the KNO_3 addition. The latter deviation from equilibrium e.m.f. thus disappears on extrapolation at an Ag^+ -ion concentration, corresponding

* Measurements at $E > 165$ mV were made in an attempt to reverse the effects at $\text{pI} = 7$ to the positive side of the p.z.c. Although by careful choice of circumstances an effect with the right direction could be observed, we considered it too small to be conclusive. This presumably is caused by the asymmetry of the adsorption isotherms around the p.z.c.,¹⁰ and the difficulties inherent in the high concentrations of potential-determining ions.

to $E = +165$ mV of our cell. The reasoning given in fig. 1 suggests that this value represents the p.z.c. of our electrodes.

In order to compare our value of the p.z.c. (165 mV against 0.1 N calomel electrode) with values reported in literature, we calculated the concentration of potential determining ions from our e.m.f. values. Following van Laar¹ and Bijsterbosch⁴ we defined $\text{pAg} \equiv -\log_{10} C_{\text{Ag}}$ by writing Nernst's law

$$E = E_{\text{Ag}}^{\circ'} - 0.058 \text{ pAg}, \text{ or } E = E_{\text{I}}^{\circ'} + 0.058 \text{ pI (20}^{\circ}\text{C)},$$

thereby including activity and diffusion potential terms in $E^{\circ'}$. By calibrating our cell with standard solutions we determined $E_{\text{Ag}}^{\circ'} = +471$ mV and $E_{\text{I}}^{\circ'} = -483$ mV

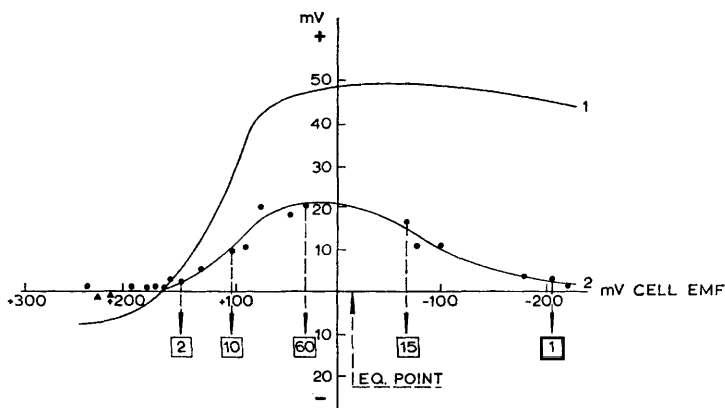


FIG. 3.—First deflection from equilibrium as a function of cell e.m.f. ●, values from experiments as described in procedure; ▲, values from experiments as described in footnote.* [], time in seconds to pass meter balance. Curve 1 gives the deflection predicted by the adsorption isotherms, if the charge remains constant (see fig. 1 and ref. (10)). Curve 2 is given by the experiments.

(at 20°C, 10⁻³ M KNO₃).³ From these values it follows that the solubility product of AgI at this temperature and KNO₃ concentration is $S = 10^{-16.3}$ in good agreement with literature data.¹¹ $E^{\circ'}$ did not differ more than 2 mV for our different types of AgI-electrode.

Having thus established the pAg-scale, we find that our $E = +165$ mV corresponds to $\text{pAg} = 5.3$. This should be compared to Bijsterbosch' $\text{pAg} = 5.33$ from electrokinetic experiments⁴ and van Laar's $\text{pAg} = 5.44$ from adsorption measurements (at 25°C).¹ The agreement seems satisfactory, especially when the different techniques of AgI preparation are taken into account. Measurements on the electrolytic and colloid electrodes showed the same pAg-dependent effects. Here $E_{\text{p.z.c.}} = 165 \pm 5$ mV.

DISCUSSION

It could be argued that the effect of inert electrolyte addition on the cell e.m.f. does not really vanish towards $\text{pAg} = 5.3$, but that it is gradually obscured by the rise of the exchange current with Ag⁺-concentration. The agreement with van Laar's and Bijsterbosch' pAg values for the p.z.c. would then be a mere coincidence.

Two observations contradict this supposition. The meter could still easily follow the changes in electrode potential when the last significant deflection was observed (e.g., $E = 160$ mV). Furthermore, according to this reasoning, the cell would reach its new equilibrium so quickly that any other effect would be drowned in the negative

sweep. The small effects at $E > 165$ mV, however, are still observed at a higher Ag^+ -concentration, indicating that the exchange current is not too high to prevent measurements.

Could the observed positive deflection be caused by a temporary diffusion potential in the poorly homogenized cell liquid? Admittedly the differences in ionic strength create diffusion potential differences, but this effect will be independent of pAg. Moreover, even in the extreme case that no mixing occurred, the extra diffusion potential could hardly exceed 1 mV since the transference numbers of K^+ and NO_3^- in KNO_3 are almost equal. We therefore conclude that the magnitude of the effect, its dependence on pAg and its reproducibility refute an explanation from diffusion potentials.

Two characteristics of the observed influence of the inert electrolyte, suddenly reaching the electrodes, on the cell e.m.f. suggest explanation in terms of fig. 1. First, the direction and magnitude of the deviation from equilibrium e.m.f. are predicted by these well-established adsorption isotherms. Secondly, the time in which equilibrium is restored depends markedly on the concentration of potential-determining ions, thereby proving the importance of the exchange current density. The third argument—suggestive but no proof—is the fact that the effect vanishes at a pAg very near the p.z.c. as determined by other independent methods. Altogether we conclude that in our measurements the exchange current fails to maintain equilibrium conditions during the rapid process, even at the “non-polarizable” AgI/electrolyte interface.

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