when 4 micrograms of iodine was present in the reaction solution.

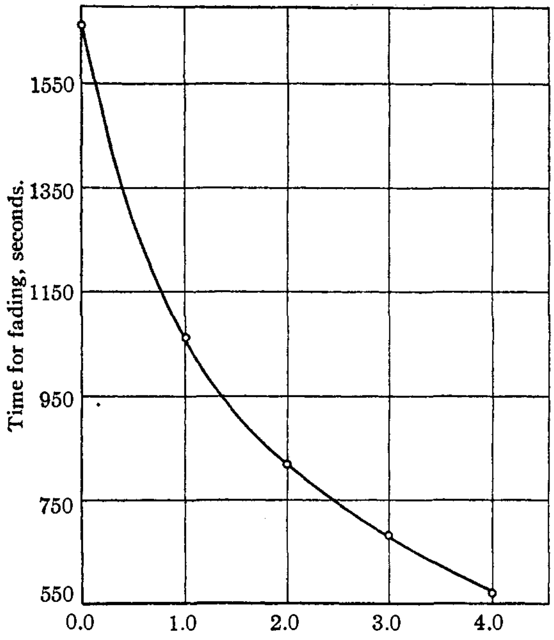

Fig. 5.

The light transmission errors, and errors due to deviation from Beer's law, for practical purposes are therefore negligible and either the colorimeter or the photoelectric cell can be used to measure the fading of methylene blue by the system.

For comparison of times for fading of methylene blue catalyzed by different concentrations of iodine a color intensity equal to 10 mm. of the standard solution of methylene blue (1 mg./100 cc.) in the movable cup of the colorimeter was chosen. When the times to reach this intensity are plotted against the corresponding concentrations of iodine, curve Fig. 5 is obtained. The method of plotting the fading curves as straight lines serves as a method of averaging the colorimetric readings.

A series of analyses carried out using this technique check within 5%.

Summary

A method for determination of iodine in sulfite solutions in concentrations up to 4 micrograms (as potassium iodide) has been devised from considerations of a system of reactions in which iodine acts as a catalyst and sulfite enters into the reaction mechanism. The method is carried out by adding hydrochloric acid and methylene blue to the sulfite solution and measuring the fading as the reaction proceeds in a specially designed apparatus.

Minneapolis, Minn. Received September 14, 1936

[Contribution from the School of Chemistry of the Institute of Technology, University of Minnesota]

Electric Potentials at Crystal Surfaces, and at Silver Halide Surfaces in Particular

By I. M. Kolthoff and H. L. Sanders[1]

With the exception of the glass electrode, very few investigators have studied the thermodynamically reversible potentials which exist at non-metallic surfaces.[2]

For various reasons a study of the potential at the interface of slightly soluble salts in equilibrium with their saturated solutions is of interest. It has been claimed by Haber[3] that this potential, π, is determined by the concentration (or, better, the activity) of the lattice ions in the solution according to the equation

$$\pi = K_c + \frac{RT}{nF}\ln a_c = K_a - \frac{RT}{nF}\ln a_a$$

in which a_c denotes the activity of the cations, and a_a that of the anions in solution. Actually Haber used ion concentrations instead of activities.

Some rough measurements[3] with silver chloride and calomel membranes were in agreement with the above equation. Recently Tendeloo[4] has made measurements with slices of minerals like heavyspar ($BaSO_4$) and fluorite (CaF_2), finding under specified conditions an approximate agreement with the foregoing equations over a limited range of concentrations.

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[1] Present address: Department of Chemistry, McGill University, Montreal, Canada.

[2] For a review of R. Beutner's work on the phase-boundary potentials between immiscible liquids see L. Michaelis, "Hydrogen Ion Concentration," Williams and Wilkins, Baltimore, Md., 1926, Chap. 8; also M. Dole, "The Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., Inc., New York, 1935, p. 380; for a review of the work of various other workers in this field see M. Cremer, "Handbuch der normalen und pathologischen Physiologie," Vol. VIII, J. Springer, Berlin, 1928, pp. 999–1053.

[3] F. Haber, *Ann. Physik*, [4] **26**, 927 (1908).

[4] H. J. C. Tendeloo, *Proc. Acad. Science, Amsterdam*, **38**, 434 (1935); *Rec. trav. chim.*, **55**, 227 (1936); *J. Biol. Chem.*, **113**, 333 (1936).

In the present paper are given the results of a more detailed study of cells involving pure silver halide membranes.

Introduction

The following cells were measured in this study

Cell I: $\text{Ag/AgX(s)}, \text{X}^-(a_1)/\underset{\text{membrane}}{\text{AgX}}/\text{X}^-(a_2)/\text{KNO}_3\text{(satd.)}/\text{KCl(satd.)}\ \text{Hg}_2\text{Cl}_2/\text{Hg}$

Cell II: $\text{Ag/AgX(s)}, \text{X}^-(a_1)/\underset{\text{membrane}}{\text{AgX}}/\text{X}^-(a_2), \text{AgX(s)/Ag}$

Cell III: $\text{Ag/AgX(s)}, \text{X}^-(a_2)/\text{KNO}_3\text{(s)/KCl(satd.)}, \text{Hg}_2\text{Cl}_2/\text{Hg}$

in which X^- represents the chloride, bromide or iodide ion, and AgX the corresponding silver halide.

The expression for the e. m. f. of cells of types I and II can be derived by considering the reactions at each phase boundary. Suppose one faraday of electricity passes through cell I from left to right. The following reactions then take place at each phase boundary in the case of a silver chloride cell

$$\begin{aligned} \text{Ag} + \text{Cl}^-(a_1) &= \text{AgCl(s)} + \text{e} \\ \text{AgCl}_{\text{memb.}} &= \text{Ag}^+_{\text{memb.}} + \text{Cl}^-(a_1) \\ \text{Ag}^+_{\text{memb.}} + \text{Cl}^-(a_2) &= \text{AgCl(s)} \\ \text{Hg}_2\text{Cl}_2\text{(s)} + 2\text{e} &= 2\text{Hg} + 2\text{Cl}^-(\text{satd. KCl}) \end{aligned}$$

The total cell reaction is therefore the sum of these partial reactions, and is

$$2\text{Ag(s)} + \text{Hg}_2\text{Cl}_2\text{(s)} + 2\text{Cl}^-(a_2) = 2\text{Hg} + 2\text{AgCl(s)} + 2\text{Cl}^-(\text{satd. KCl})$$

The equilibrium constant of this reaction is

$$K' = (a\text{Cl}^-)^2_{\text{satd. KCl}}/(a\text{Cl}^-)^2_2$$

Since the activity of the chloride ion in the saturated potassium chloride is constant, the equilibrium constant becomes

$$K = 1/(a\text{Cl}^-)^2_2$$

and the equation for the e. m. f. of cell I is then

$$\begin{aligned} E &= RT/2F \ln K + RT/2F \ln (a\text{Cl}^-)^2_2 \\ &= E^0 + RT/F \ln (a\text{Cl}^-)_2 \end{aligned}$$

It is readily shown that $E^0 = E_{\text{S.C.E.}} - E^0_{\text{AgCl}} = 0.246 - 0.222 = 0.024$ v.

whence
$$\begin{aligned} E &= 0.024 + RT/F \ln (a\text{Cl}^-)_2 \\ &= 0.024 - 0.0591\ p(\text{Cl}^-)_2\ (25°) \end{aligned}$$

For cells of type I, then, if we neglect the small liquid junction potential between the saturated calomel reference electrode and the halide solution, the relation between the e. m. f. and $p(X^-)_2$ should be a straight line with slope equal to RT/F and intercept equal to the difference in e. m. f. between the saturated calomel electrode and the corresponding silver–silver halide electrode, provided there is no asymmetry potential.

It is derived from the same considerations that the e. m. f. of cells of type II should be zero at all concentrations of the halide solutions on each side of the membrane, if there is no asymmetry potential across the membrane.

Cells of type III serve to measure the actual pX value of the solutions in contact with the membrane.

The derivation of the above equation involves chloride going into solution on the left side of the membrane and deposition of chloride from the solution on the right side of the membrane in the form of silver chloride. Apparently, then, in order for cells of this type to function reversibly, one or both of the lattice ions must be able to migrate in the solid. If this condition is not fulfilled, cells of the above type cannot function.

It should be emphasized that the foregoing derivation does not involve any assumption with regard to the individual potential differences (π) at the interface on each side of the membrane, which of course are impossible to measure.

Experimental

Apparatus.—In order to overcome the high resistances in some of the systems investigated, and to eliminate possible polarizing currents from the potentiometer, an electron tube voltmeter was constructed. The design of the instrument was similar to those described by Greville and Maclagan,[5] Dubois[6] and others. An FP54 General Electric pliotron tube was used, together with a sensitive galvanometer, rated at 27,000 megohms. The method of floating grids was not employed. Tests showed that e. m. f.'s could be read to 0.1 mv. through resistances of several hundred megohms.

All measurements were made in an air-bath, held at 25.0 ± 0.1°. The bath also served to shield the silver salts from excessive exposure to light.

Materials.—Most of the work was carried on with the silver halides. For their preparation Mallinckrodt analytical grade silver nitrate proved sufficiently pure, melting without any trace of darkening—a delicate test. For preparing silver chloride, redistilled hydrochloric acid was used.

The preparation of the silver halides was carried out by slowly adding tenth molar silver nitrate solution to tenth molar halide solution in a dim red light. Conductivity water was used throughout. Occlusion of traces of silver nitrate by the silver halide results in discoloration of the latter upon fusion, but this is prevented by the use of dilute solutions. The precipitated halide was washed repeatedly by decantation.

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(5) G. D. Greville and N. F. Maclagan, *Trans. Faraday Soc.*, **27**, 210 (1931).

(6) D. Dubois, *J. Biol. Chem.*, **88**, 729 (1930).

The standard silver–silver halide electrodes used were made by silver plating platinum electrodes, then making these anodes in the appropriate tenth molar halide solution.

Silver Halide Diaphragms.—Several methods for making impermeable silver halide "electrodes" were tried. They could not be blown into bulbs like glass, nor could they be coated over glass bulbs. The Haber[3] method of melting some of the salt in the bend of a U-tube gave leaky plugs. Finally the problem was solved by melting the salt in a clean porcelain crucible in a small electric oven. The solidified melt, in disk form, about five millimeters thick, could be removed after soaking in water. These disks were then fastened over one end of a 10-mm. glass tube with sealing wax. Some 0.01 *M* halide solution (a_1) was poured in, and a standard silver–silver halide electrode inserted. This arrangement is termed the "crystal electrode" and is reminiscent of a MacInnes and Dole membrane glass electrode. Disk resistances were of the order of ten megohms.

In practice, our procedure was to immerse a standard silver–silver halide as well as several crystal electrodes in a solution, then measure each of these against a saturated calomel half-cell, using a saturated potassium nitrate salt bridge. The value of a_2 in cell I was varied by adding silver nitrate or sodium halide to the outer solution. In each case the value of a_2 (plotted as *p*X) was determined by measuring the e. m. f. between the ordinary silver halide electrode in the solution and the saturated calomel electrode, using cell III.

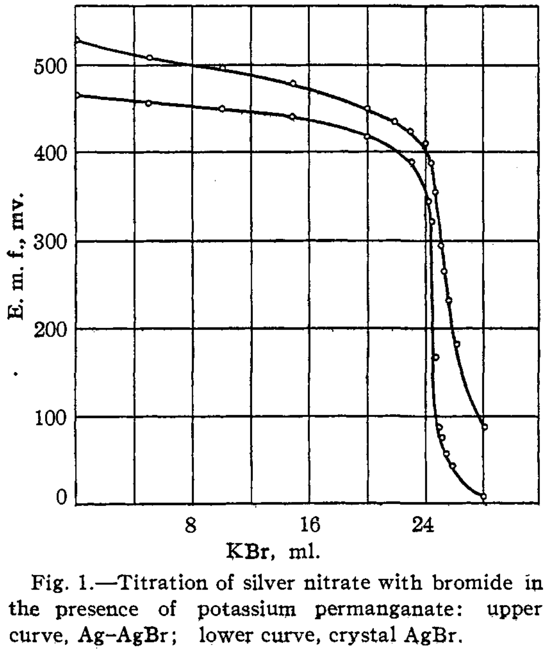

Fig. 1.—Titration of silver nitrate with bromide in the presence of potassium permanganate: upper curve, Ag–AgBr; lower curve, crystal AgBr.

Since the total e. m. f. of cell II is zero, it follows that cells I and III should have identical e. m. f. values provided that a_2 is the same in each, and there is no asymmetry potential across the membrane. Stated in other words the standard silver–silver halide electrode should give the same reading as a composite crystal electrode.

Experimental Results

Table I gives the results found on the first trial of the crystal silver chloride electrodes. The disk used had a very low asymmetry potential. Later readings were made to four decimal places.

TABLE I

COMPARISON OF SILVER CHLORIDE STANDARD AND CRYSTAL ELECTRODES

AgNO$_3$ soln. (approx.), *M*	E. m. f.	
	Standard AgCl No. 6 (Cell III)	Crystal AgCl No. 2 (Cell I)
10^{-5}	0.279	0.280
10^{-4}	.339	.337
10^{-3}	.384	.381
10^{-2}	.453	.453
10^{-1}	.500	.500

Although, as we have pointed out, this agreement was to be expected, the objection might be raised that it was found only because a film of metallic silver had formed on the supposedly pure salt disk by accidental reduction. That this was not the case is shown by the following considerations. (1) The silver chloride disks were perfectly clear and transparent with no discoloration whatever visible. (2) On adding potassium permanganate to the solution the potential of the disk remained constant, but that of a standard silver chloride electrode changed by over 100 mv. due to an oxidation potential being set up at the metallic silver. When a disk was purposely reduced superficially with tin and hydrochloric acid, it then became sensitive to permanganate. (3) On soaking a standard and a crystal electrode in platinic chloride solution overnight, the former was spoiled, due to separation of platinum onto the silver, but the latter was unaltered. (4) A silver nitrate solution was titrated with potassium bromide in the presence of permanganate, using both standard and crystal silver bromide electrodes. As Fig. 1 shows, the former gave higher e. m. f. readings than the latter, and the break in potential at the equivalence point was less pronounced with the standard electrode, due to secondary effects.

These permanganate tests were not so conclusive in the case of crystal silver iodide electrodes, perhaps due to oxidation of the salt itself.

In Fig. 2 are shown graphically the main results of this investigation. In it the e. m. f. of cell I is plotted against the *p*X value of the solution. These curves are not averaged values, but are typical runs. At least six electrodes of each kind were prepared, and several runs made with each. Though the asymmetry potentials changed several millivolts between runs, all satisfactory electrodes showed a constant linear relation on consecutive runs. About four out of five of the crystal electrodes prepared were considered satisfactory.

Equilibrium potentials were established very quickly whether or not the solution around the electrode was pre-saturated with the appropriate silver halide; in most of the runs it was saturated, however.

The silver chloride line had a slope of 0.0579, the silver bromide of 0.0574—both slightly less than the theoretical value of 0.0591 at 25°. With silver iodide, the precision was not as great as with the other two electrodes, as seen by Fig. 2. In this case the slope of the line was 0.052.

If these lines are extrapolated to $pX = 0$, the following values for the cell E^0 are found: E^0(AgCl) = +0.020 v.; E^0(AgBr) = +0.160 v.; E^0(AgI) = +0.380 v. Taking the potential of the saturated calomel electrode as 0.246 v., the following are the calculated values: E^0(AgCl) = +0.024 v.; E^0(AgBr) = +0.175 v.; E^0(AgI) = +0.398 v.

The agreement between the experimental and calculated values is very good in the case of silver chloride membranes, indicating that the asymmetry potential is very small (4 mv.); in the case of silver bromide, the asymmetry potential was usually found to be of the order of 15 mv., and with silver iodide of 18 mv. The asymmetry potentials depend upon the method of preparation and the age of the membranes, their magnitude decreasing with age.

Certain writers seem to have thought that pure silver halide electrodes may be obtained by coating a platinum wire with the salt. Thus Hiltner[7] melted silver chloride round a platinum wire using a blast lamp flame, and found satisfactory behavior. We carefully melted silver bromide about a silver wire in the electric oven. The cooled mass was clear, the imbedded length of the wire being plainly visible through the transparent salt. Such a "rod" type of electrode showed a fluctuating and indefinite potential, which changed greatly on mere agitation of the solution. Similar results were found with silver chloride. Since the silver halides are not electronic conductors they naturally cannot behave as metallic electrodes because no reversible electron reaction can occur at their surface.

Finally, the effects of various ions on the crystal electrode potentials were studied. In a solution saturated with potassium nitrate the silver bromide membrane electrode cells again gave linear e. m. f.–pX curves at all concentrations of bromide ion used, the slopes being about the same as those found in the absence of the nitrate. The silver chloride membrane cells showed no changes in potential upon addition of small amounts of hydrogen, lead or thallous ions. Ions which are supposedly potential-determining, like chloride and bromide, failed to affect the potentials of the silver iodide membranes under conditions at which no chemical precipitation could occur.

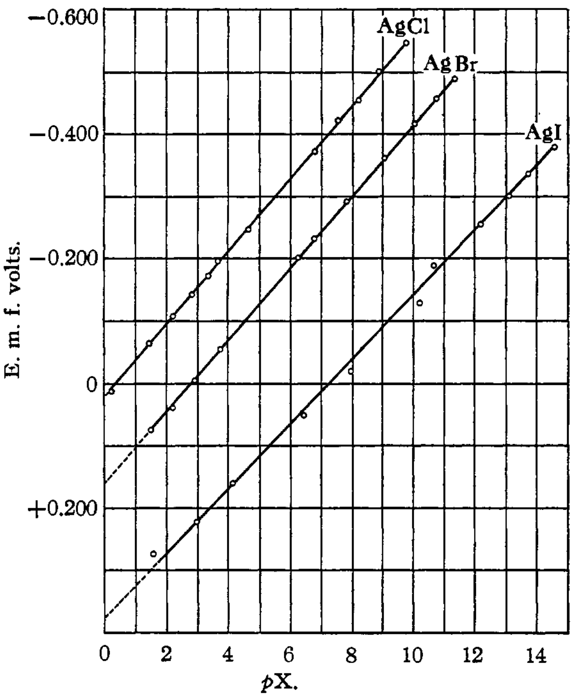

Fig. 2.—Change of potential of silver halide surfaces.

Following much the same technique as above, an attempt was made to duplicate the results of Haber with paraffined calomel tablets, and of Tendeloo with heavyspar and fluorite, but with no success, the observed potentials being unreproducible, and changing upon the addition of any ion. Our results with the fluorite electrode are in agreement with those reported recently by Anderson[8] who, contrary to Tendeloo, found that the calcium fluoride membrane did not function as a calcium electrode.

It is hoped to extend this work and discuss some of its theoretical implications in the near future.

Acknowledgment.—The junior author wishes

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(7) W. Hiltner, "Ausführung potentiometrischer Analysen," Verlag Julius Springer, Berlin, 1935.

(8) R. S. Anderson, *J. Biol. Chem.*, **115**, 323 (1936).

to express his gratitude to McGill University, Montreal, for its award of the Moyse Travelling Scholarship, which enabled him to do this work. We are particularly indebted to Professor F. H. MacDougall for his aid in the derivation of the equations presented in the first part of this paper.

Summary

An expression has been derived for the e. m. f. E of cells involving silver halide membranes, of the type

$$\mathrm{Ag/AgX(s),\ X^-}(a_1)\mathrm{/\underset{membrane}{AgX}/X^-}(a_2)\mathrm{/KNO_3(sat.)//KCl(sat.),\ Hg_2Cl_2/Hg}$$

It was found that

$$E = E^0 + RT/F \ln (a_2)$$

The experimental results obtained with fused silver halide membranes over a wide range of values of a_2 showed that $E = E^0 + A \ln(a_2)$ in which A was found to be slightly less than the theoretical value.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 3, 1936

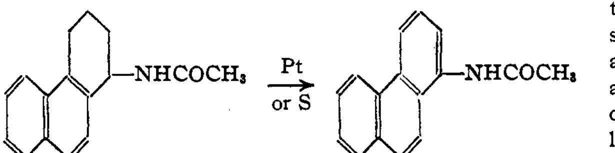
NOTES

A New Synthesis of 1-Aminophenanthrene

BY W. E. BACHMANN

Recently[1] we described the preparation of 1-aminophenanthrene, starting from phenanthrene. This new phenanthrylamine can also be obtained from naphthalene through the intermediate compound, 1-keto-1,2,3,4-tetrahydrophenanthrene. The oxime of this cyclic ketone is reduced by sodium amalgam and alcohol to 1-amino-1,2,3,4-tetrahydrophenanthrene[2] and the acetyl derivative (I) of the amine is dehydrogenated to 1-acetylaminophenanthrene (II). The free base, 1-aminophenanthrene, can be obtained by hydrolysis of the acetyl derivative.

Complete dehydrogenation of 1-acetylamino-1,2,3,4-tetrahydrophenanthrene takes place rapidly when the compound is heated with half its weight of platinum black at 320°; the 1-acetylaminophenanthrene is obtained pure by a single recrystallization from benzene. We have also employed sulfur for the dehydrogenation; with this reagent some oily by-products are formed in the reaction, but the 1-acetylaminophenanthrene can be isolated in pure form in yields of 50–60%.



(I) (II)

Experimental

1 - Acetylamino - 1,2,3,4 - tetrahydrophenanthrene.—A mixture of 13 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene,[3] 6 g. of hydroxylamine hydrochloride and 8 cc. of pyridine in 80 cc. of absolute alcohol was heated on a steam-bath for three hours. The solution was evaporated to dryness and the residue was digested with water. The oxime, which was formed in quantitative yield, was filtered off and when dried was sufficiently pure for the next step.

A mixture of 13 g. of the oxime and 180 cc. of alcohol was warmed to 50–60° and treated with 150 g. of 2% sodium amalgam in portions in the course of half an hour. Throughout the reaction the temperature was kept below 60° by external cooling and the solution was kept acidic by addition of acetic acid. Any sodium acetate that precipitated was brought back into solution by addition of small amounts of water. When the reaction was complete, the solution was separated from the mercury and the alcohol was evaporated. The residue was taken up in water and a small amount of oily impurities was removed by extraction with carbon tetrachloride. The aqueous solution was made alkaline and the 1-amino-1,2,3,4-tetrahydrophenanthrene was extracted by benzene. Evaporation of the benzene left the amine as an oil which quickly solidified. A mixture of the crude amine and 15 cc. of acetic anhydride was refluxed for five minutes. The acetic acid and the excess of acetic anhydride were removed by directing a jet of air onto the warm solution. The crystalline residue of the acetyl derivative was digested with cold acetone and the colorless crystals were filtered off; yield, 10 g. 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene crystallizes from acetone in colorless needles; m. p. 176°. The compound is not very soluble in cold acetone but dissolves in benzene and in acetic acid.

Anal. Calcd. for $C_{16}H_{17}ON$: N, 5.9. Found: N, 6.0.

Dehydrogenation of 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene.—A mixture of 10 g. of 1-acetylamino-1,2,3,4-tetrahydrophenanthrene and 2.5 g. of sulfur was

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[1] Bachmann and Boatner, THIS JOURNAL, 58, 2097 (1936).

[2] Our experiments on the preparation of this compound were already completed at the time Burger and Mosettig [*ibid.*, 58, 1570 (1936)] reported its preparation by the same method.

[3] Haworth, *J. Chem. Soc.*, 1128 (1932).