

The Specific Electrode Potential of Bismuth

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Bismuth is one of the most important metals the specific electrode potential of which is not accurately known. The experimental determination of this is rendered difficult by the fact that in the case of bismuth the simple salts, such as the chloride, nitrate, and sulfate, which are usually employed in such determinations, are strongly hydrolysed in solution forming insoluble basic compounds.

Previous Work.

¹
Neuman determined the potential of bismuth against solutions of the chloride, nitrate, and sulfate². Owing to the uncertainty of the concentration of the bismuth-ion in these solutions, he made no attempt to calculate the specific electrode potential.

1. Bernhard Neuman, Zeit. Phys. Chem. 14, P.193, 1894
2. Obtained by adding the chloride, nitrate and sulfate to water in the proper amounts to make one molal solutions, and filtering off the precipitated basic salt.

Foerster and Schwabe¹ measured the potential of bismuth against a 0.65 normal solution of bismuth fluosilicate, $\text{Bi}_2(\text{SiF}_6)_3$. The value found, referred to the hydrogen electrode, was -0.295 volt#. Again, because of uncertainty in the ion concentration in this solution, the specific electrode potential was not calculated.

The value given in most elementary text books² is -0.39 volt#³. This value is used by Palmer⁴ in his discussion of "Electrolytic Potentials and the Periodic System". In all these references the value given is followed by a question mark. Abegg, Auerbach,⁵ and Luther, in their recent compilation of electromotive force data and in a later supplement, give the value -0.2 volt#.

1. F. Foerster and E. Schwabe, Zeit. fur Electrochem. 16, P.280, 1910.
2. Alexander Smith, Inorganic Chemistry (1910) W.A. Noyes, Textbook of Chemistry (1913).
3. All electrode potentials in this paper are referred to the Molal Hydrogen electrode. The electrode potential is considered positive when positive electricity tends to flow from the electrode to the solution.
4. Nernst's Festschrift, 336 (1912).
5. Messungen elektromotorischen Krafte galvanischer Ketten mit wasserigen Elektrolyten, R. Abegg, Fr. Auerbach and R. Luther. (1911)

This discrepancy seems to be due to the fact that the value given in the text books was apparently taken from a compilation by Wilsmore,¹ who recalculated the data of various investigators. He gives the specific electrode potential of bismuth as less than -0.391, basing his calculations on data of Neuman.

Unfortunately, Wilsmore gave the wrong sign to the bismuth cells measured by Neuman. Neuman found the electromotive force of the cell:

Bi, BiCl₃(saturated sol.), Indifferent electrolyte,
KCl (1.0M.), Hg₂ Cl₂+ Hg.

to be 0.145 volts. Taking the "absolute" potential of the normal calomel electrode to be -0.560 he made the following addition:

Bi, BiCl ₃ // Normal Calomel.....	+ .145
Normal Calomel // Absolute Zero	<u>-.56</u>
Bi, BiCl ₃ // Absolute Zero	-.415 volts

Taking this same data Wilsmore calculated as follows:

Bi, BiCl // Normal Calomel	-.145
Normal Calomel // Molal Hydrogen	<u>-.383</u>
Bi, BiCl // Molal Hydrogen	-.428 volts.

1. N.T.M. Wilsmore, Zeit. Phys. Chem. 35, 316, 1900.

This is the value from which he calculated the specific electrode potential of bismuth to be less than -0.39^1 .

The chief difficulty in determining the value of the specific electrode potential of bismuth is due, as has been pointed out, to the uncertainty of the ion concentration in the solutions of bismuth salt. The common salts of the tri-univalent type, such as the chloride, nitrate, etc., which are commonly employed in determinations of this kind, give insoluble hydrolysis products, while the degree of ionization of the more complex salts is very uncertain. The perchlorate, however, offers peculiar advantages for this determination, since it does not give insoluble hydrolysis products at moderate concentrations.

1. That Wilsmore used the same sign convention as Neuman is evident from the following:

Neuman measured the potential of the cell
Ag, AgNO₃ (1M), Indifferent electrolyte (1M),
K Cl (1M.) $\text{Hg}_2\text{Cl}_2 + \text{Hg}$.

and found it to be -0.495 volts. He then made the following addition:

Ag, AgNO	//	Normal Calomel	$-.495$ volts
Normal Calomel	//	"Absolute" zero	$-.560$
Ag, AgNO	//	"Absolute" Zero	-1.055 volts

The present determination was carried out by measuring the electromotive force of a bismuth electrode, in a solution of bismuth perchlorate and perchloric acid, against a hydrogen electrode, in a solution of perchloric acid of approximately the same concentration.

To check the above determination the equilibrium of the bismuth-ion, cupric-ion, metallic bismuth and metallic copper was investigated.

Preparation of the Chemicals.

The perchloric acid was obtained from the Genessee Chemical Works. It gave no test for chlorides, sulfates or iron, and left no residue when evaporated to dryness. Chlorates were present ~~valent~~ in small amounts. The strength of the solutions was determined by titrating ~~the~~ ^{with} standard sodium hydroxide.

(Note continued)

Using this data Wilsmore calculated as follows:

Ag, AgNO ₃ // Normal Calomel	-.495
Normal Calomel // Molal Hydrogen	<u>-.283</u>
Ag, AgNO ₃ // Molal Hydrogen	-.778 volts.

From this Wilsmore calculated the value of the specific electrode potential to be less than -.780 volts. This agrees with recently determined values.

The bismuth was made by electrolytic precipitation from a strong solution of bismuth chloride in six normal hydrochloric acid, between platinum anodes and cathodes, and using a high current density. The metal was precipitated as a loose, spongy mass, which fell off the electrodes at intervals and sank to the bottom of the vessel. The metal was ground in a mortar with dilute nitric acid, and then washed with water. The washing was repeated until ^{some time after} the wash-water no longer showed traces of chlorides.

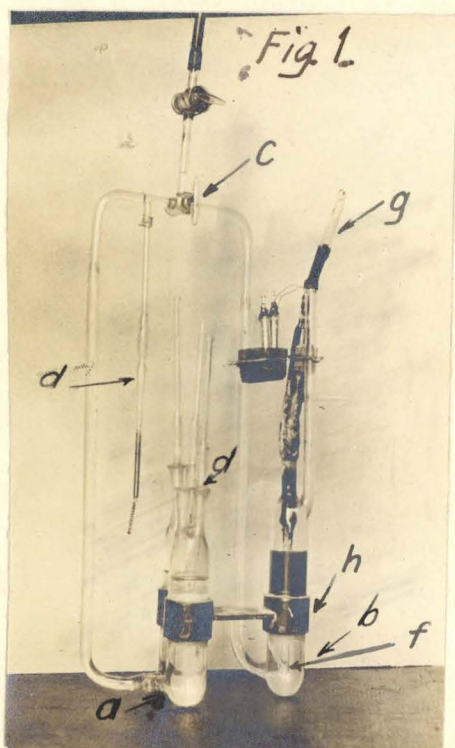
The metallic bismuth was converted into the oxide by heating in an open porcelain dish.

The bismuth perchlorate was obtained by heating the bismuth oxide with perchloric acid. The first solutions were made by dissolving the metal in perchloric acid, but it was found that it was necessary to evaporate the acid until it was very concentrated, in order to dissolve the metal at all rapidly. At such concentrations the acid is unstable, and on several occasions it exploded violently. The solubility of bismuth perchlorate in one-tenth normal perchloric acid was less than 0.02 normal. Since solutions weaker than 0.001 normal could not be analyzed accurately, the ^{range of} concentrations over which measurements could be made was very limited.

Hydrogen was made by the electrolysis of an alkaline solution of sodium sulfate. The gas was passed through potassium pyrogallate, acid dichromate and finally through perchlorate^{ic} acid of the same strength as that used in the cell. This last was in a saturator attached to the cell and rocked with it in the thermostat.

Description of Apparatus.

The bismuth cell (Figure 1) (a) consisted of two compartments connected together at the bottom. Each compartment was provided with two hollow ground glass stoppers (d). To the upper portion of these, tubes



were sealed to allow the cell to be submerged in the thermostat. To the lower end of one of the stoppers in each compartment, a tube was sealed extending to the level of the liquid. Into the lower end

of this tube was sealed a platinum spiral.

The bismuth electrodes were made by depositing bismuth on the platinum spirals. It was found that the most coherent coats were obtained by plating from a weakly acid solution (about 0.05 normal), using a current density of not more than 0.005 amperes per square centimeter and a temperature of about 60 °C. Electrodes thus prepared from the bismuth oxy-chloride, made in the purification of the bismuth chloride described above, agreed with those made from bismuth perchlorate and Kahlbaum's bismuth nitrate within 0.0005 volts, which was as closely as electrodes prepared from the same solution agreed with each other. Since adherent coats could be more easily contained from the nitrate and the perchlorate than from the chloride, all electrodes used in the final measurements were made from solutions of these salts.

The open stoppers in the two compartments allowed air to be drawn in and expelled when the cell was rocked, thus enabling the liquid to surge from one chamber to the other. The rise and fall was about one-half to three-quarters of an inch, and the rate of rocking was 40 cycles per minute. In this way ample stirring of the solution was obtained.

The hydrogen cell (b) had but one compartment. The hydrogen electrodes were made by platinizing platinum foil. No lead acetate was used in this operation as it appears to be unnecessary and may be a source of error. After a good coating had been deposited, sulphuric acid was poured into the cell and the current commutated at five minute intervals for about 40 minutes, then at minute intervals for 20 minutes. After one or two preliminary runs had been made the difference in potential between the electrodes thus prepared was less than 0.00001 volts. Hydrogen was bubbled over the electrodes from a capillary tube (f) which extended almost to the bottom of the cell. It then escaped through the outlet tube (g).

The hydrogen cell was connected to the bismuth cell by the siphon tube (c). At the top of this was a three-way stop-cock (c) to whose third arm a second stop-cock was sealed. The three-way stop-cock was kept closed during the determinations to prevent diffusion. It was not greased and the film of liquid around it afforded ample conductance for the minute current required to make the measurements.

The cells were cemented into a brass holder (h) with glycerine and litharge cement. The whole cell was supported by a brass rod (r) which was bolted

to the holder. A clamp attached to this and loosely screwed to a rod above the thermostat formed a hinge on which the cells could be rocked.

All electrical connections were made by means of mercury cups, each electrode having a separate cup.

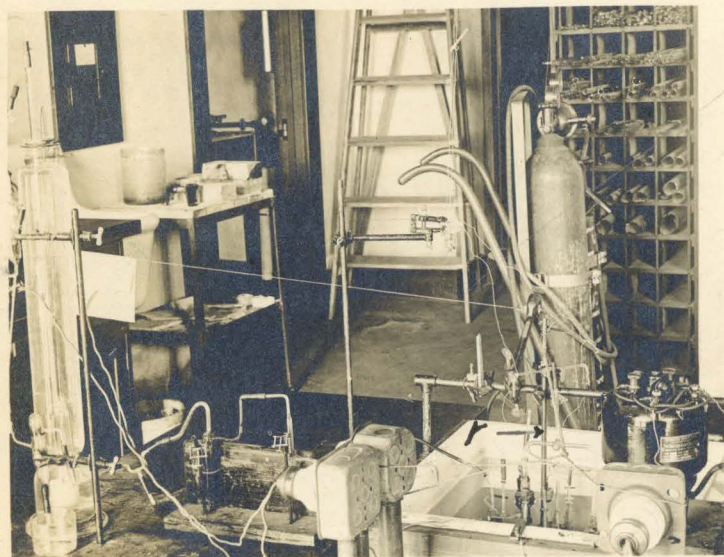


Fig. 2

affected the potentiometer, so while readings were being taken the current was turned off.

Figure 3 shows the general arrangement of the apparatus. The

Figure 2 shows the position of the cell in the thermostat, the saturators and the hydrogen generator. The motor in the right foreground is the thermostat stirrer. It was found that when this was running it

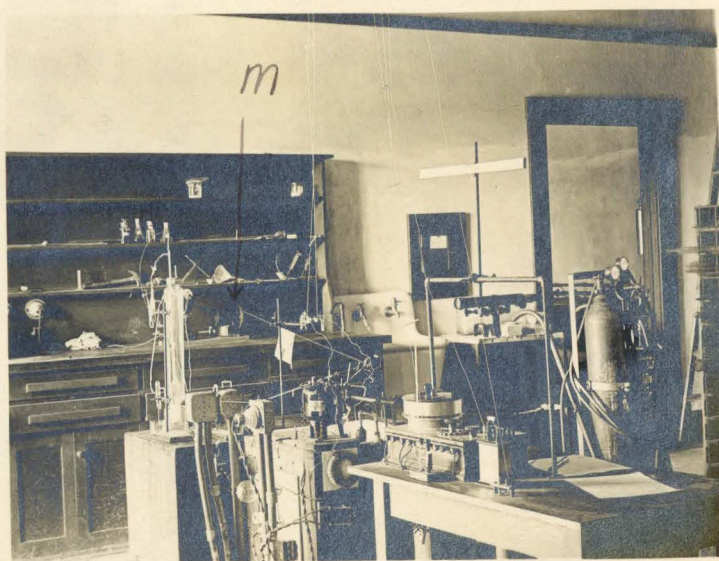


Fig. 3

motor (m) which rocked the cell was placed at a distance, so that this could be kept running while measurements were being made.

The electrical measurements were made by means of a Leeds and Northrup potentiometer (No.34346), used in conjunction with a galvanometer² of the D'Arsonval type (No.34459) and a Weston standard cell (No.3528). This cell agreed with one calibrated³ by the Bureau of Standards within 0.00005 volts.

As a considerable quantity of bismuth dissolved off the electrodes during a run, it was necessary to analyse the solutions at its conclusion. This was done by pipetting a definite quantity of solution from the cell, adding standard hydrochloric acid, and titrating ~~the~~^{with} sodium hydroxide. The precipitated bismuth oxy-chloride was then filtered off in weighed Gooch crucibles, dried at 110 C and weighed. The acidity found by this titration was too high by twice¹ the number of moles of the basic salt formed.

Hence, to obtain the true acidity, this quantity was subtracted from the acidity found by the titration.



2. Also made by Leeds & Northrup.

3. Thermo-electric effects were corrected for by shortcircuiting the leads at the cell, placing them in the same mercury cup. This correction was found to be entirely negligible.

To test this method, samples of bismuth weighing 0.0412 grams and 0.0428 grams, respectively, were dissolved in nitric acid and the excess of acid evaporated off. An excess of hydrochloric acid was added, and then a solution of sodium hydroxide, until the solution was neutral to methyl orange. The precipitated bismuth oxy-chloride weighed 0.0514 and 0.0532 grams, respectively, which is the equivalent of 0.0412 and 0.0426 grams of the metal. This showed that the precipitation of bismuth in this manner was sufficiently accurate for the purpose. Precipitation as a sulphide, carbonate and electrical precipitation as a metal were tried. The first two methods were less convenient, and the latter was less accurate.

Procedure.

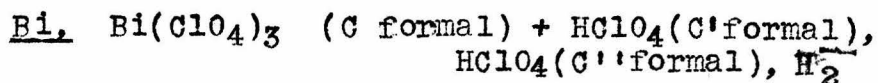
The hydrogen side of the cell was washed thoroughly four times with perchloric acid of the strength used in the determination, and then filled until the solution almost covered the electrodes. Next, pressure was applied by blowing on the hydrogen outlet tube, thus forcing the liquid up the siphon tube. When the arm of the siphon was completely filled, the three-way stop-cock was quickly turned, shutting off the hydrogen cell completely.

The bismuth cell was then rinsed four times and filled. The solution was drawn up into the siphon and through the three-way stop-cock and the upper stop-cock was closed. Hydrogen was then run into the cell for at least three hours to saturate the perchloric acid and displaced the air in the cell. The bismuth electrodes were inserted and the joints sealed with paraffin. The cell with the pre-saturator attached to it was placed in the thermostat and rocked. In about an hour the electromotive force of the cell was steady. This slowly increased as the bismuth dissolved off the electrode and consequently the concentration of the bismuth-ion around the electrode increased. The rate of dissolving depended on the concentration of the bismuth perchlorate already present. The rate of increase of the electromotive force never exceeded 0.001 volts per hour. When a steady rate of increase was reached, readings were taken and the bismuth electrodes removed immediately to prevent more bismuth from dissolving.

The bismuth perchlorate solution was then taken from the cell and analysed for bismuth perchlorate and perchloric acid, in the manner described above. For several runs the solution in the hydrogen cell was also analysed, but since no appreciable change

was detected in the concentration of the perchloric acid, this practice was discontinued.

The cell measured may be represented as follows:



The measured electromotive force is the algebraic sum of the potential set up by the bismuth electrode and the solution of its ions, of that due to the liquid junction, and of that at the hydrogen electrode. The hydrogen electrode was corrected to the normal hydrogen electrode in the usual manner, taking into account the pressure of the water vapor above the solution and the barometric pressure.

Since the concentration of the perchloric acid is large compared with that of the bismuth perchlorate, the liquid junction is practically that due to the two acid solutions. The liquid potential is then given by the formula:

$$E_{\text{liq.}} = \frac{\Lambda_{\text{H}^+} + \Lambda_{\text{ClO}_4^-}}{\Lambda_{\text{H}^+} + \Lambda_{\text{ClO}_4^-}} \ln \frac{C'' \gamma''}{C' \gamma'}$$

The liquid potentials thus calculated were always less than 0.01 volt and were probably correct to two millivolts.

The specific electrode potential was then calculated from a bismuth electrode potential referred to the normal hydrogen electrode.

No data could be found concerning the ionization of bismuth salts so the ionization of bismuth perchlorate was assumed to be the same as that of lanthanum nitrate ($\text{La}(\text{NO}_3)_3$).¹ In allowing for the excess of perchlorate ion from the perchloric acid, the rule that the ionization of a mixture of salts depends only on the concentration of the common ion, was employed. The ionization was therefore assumed to be that of lanthanum nitrate at a concentration equal to the sum of the concentrations of bismuth perchlorate and perchloric acid. The ionization of the perchloric acid in the hydrogen cell was calculated from Ostwald's² conductance data for that acid.

The complete calculation may be expressed thus:

$$\text{E.M.F.} = (E_{\text{Bi}}) - \left(\frac{R \cdot T}{N \cdot F} \ln C_{\text{Bi}^{+++}} \right) + \left(\frac{R \cdot T}{F} \ln C_{\text{H}^+} \right) + \left(\frac{R \cdot T}{2F} \ln \frac{760}{P_{\text{H}_2}} \right) - \left(\frac{\lambda_{\text{H}^+}^- \lambda_{\text{ClO}_4}^-}{\lambda_{\text{H}^+}^+ \lambda_{\text{ClO}_4}^-} \ln \frac{C_{\text{H}^+}^+}{C_{\text{H}^+}^-} \right)$$

1. Noyes and Johnson, J. Am. Chem. Soc. 31, P. 987, 1909
2. Landolt, Bornstein & Roth, Tabellen, 4 Auflage, Seite 1112 (1912).

The details of the five determinations, and the specific E.M.F.s calculated from each are given in

Table I.

TABLE I

Run	Electrodes From	Bismuth Cell Mols/Litre				Hydrogen Cell	
		Bi(ClO ₄) ₃	Bi ⁺⁺⁺	HClO ₄	H ⁺	HClO ₄	H ⁺
1	Bi(NO ₃) ₃	.0042	.00286	.060	.057	.079	.0745
2	do.	.0157	.0097	.120	.112	.079	.0745
3	Bi(ClO ₄) ₃	.0151	.00935	.121	.113	.0795	.0746
4	do. and Bi(NO ₃) ₃	.0014	.0009	.0795	.0746	.079	.0745
5	Bi(NO ₃) ₃	.0014	.0010	.0795	.0746	.079	.0745

Run	Barometer	Meas. E.M.F.	Liquid Potential	H ₂ Pressure Correction	\bar{E}_{Bi} Spec. Elec. Potential
1	745	- .3120	+ .0046	-.0006	-.291
2	745	- .3166	+ .0070	-.0006	-.297
3	745	- .3149	- .0071	-.0006	-.296
4	745	- .3121	0	-.0006	-.306
5	745	- .3088	0	-.0006	-.302

Mean Value -.298 volts.

The second method of determining the specific electrode potential of bismuth was based on the principle that when a solution containing the ions of two metals is in contact with these two metals, equilibrium is established when the ion concentrations are such that the electromotive forces set up by these metals and the solution of their ions are equal. Those metals whose specific electro^{de} potentials have almost the same value will therefore come to such an equilibrium that ions of both metals are present in determinable amounts.

Method

A glass stoppered bottle containing a slightly acid solution of cupric perchlorate, solid bismuth oxide, cupric oxide, metallic bismuth and metallic copper, was sealed with paraffin, placed in the thermostat and rocked for four days at a temperature of 25 C.

1. The copper perchlorate was made by heating Kahlbaum's cupric oxide with dilute perchloric acid. For the metal Kahlbaum's reduced powdered copper was used. Bismuth and bismuth oxide were prepared in the same manner as for the electromotive force determination.

At the end of this time it was found that all the metallic bismuth had dissolved and that a considerable quantity of a white amorphous powder (probably bismuth basic perchlorate) had precipitated. The solution was then filtered, a little dilute perchloric acid added, and put back into the thermostat with a new supply of finely divided metallic bismuth and copper. When it had been rocked for three days more in the thermostat, the solution was removed, filtered and analyzed for bismuth and copper.

Analyses

The bismuth was precipitated as the oxy-chloride in the manner described above (Page 11). The precipitate was then filtered off in weighed Gooch crucibles, dried at 110 °C. and weighed. The filtrate then contained about two milligrams of copper per 100 cubic centimeters of solution and about the same amount of bismuth. (This loss of bismuth is negligible). The presence of this bismuth rendered the usual methods of gravimetric analysis impracticable. Ammonia was therefore added to the solution, thus forming the complex ion $\text{Cu}(\text{NH}_3)_4^{++}$ which has a clear blue color. *colorimetric* By comparison with standard solutions the concentration of the copper could be estimated to within six or eight

1
per cent.

Results

The results of two independent runs are given in Table 2. The specific electrode potential was calculated by the equation:

$$\bar{E}_{\text{Cu}} - \frac{R}{N} \frac{T}{F} \times \text{Ln (Concentration cupric-ion)} = \bar{E}_{\text{Bi}} - \frac{R}{N} \frac{T}{F} \times \text{Ln (Concentration Bismuth-ion)}$$

The specific electrode potential of copper (to cupric-ion solution) was taken as -0.35^2 . The ionization of bismuth perchlorate was assumed to be the same as that of lanthanum nitrate and that of cupric perchlorate to be that of barium chloride.

1. An error of 10 per cent in the concentration of copper would make a difference of 0.002 volts, in the final result.

The cuprous-ion is negligible since the value of the ratio $\frac{\text{Concentration Cu}}{(\text{Concentration Cu})^2}$

calculated from the specific electrode potentials

$\text{Cu, Cu}^{++} (1M)$ and $\text{Cu, Cu}^+ (1M)$ is greater than 100,000.

2. G.N.Lewis and W.N.Lacy, J.Am.Chem.Soc.36, 804-10, (1914)

The value -0.35 was obtained from the cell $\text{Cu, Cu}^{++} // \text{SO}_4^-, \text{Hg SO}_4 + \text{Hg}$.

TABLE II

Run	$\text{Bi}(\text{ClO})_4$	Bi^{+++}	$\text{Cu}(\text{ClO})_4$	Cu^{++}	E _{Bi}
1	.0517	.0316	.00070	.00056	.283
2	.0456	.0278	.00055	.00044	.282

This result agrees fairly well with the value obtained from the electromotive force determination.

Note 2, continued from Page 19.

For the cell $\text{Cu}, \text{CuSO}_4(.005\text{M.}), \text{CuSO}_4(.05\text{M.}), \text{MgSO}_4(.05\text{M.}), \text{KCl}(.1\text{M.}), \text{KCl}(1\text{M.}), \text{Hg}_2\text{Cl}_2 \text{ Hg}$

The value was found to be -0.33 . This was considered less accurate owing to the uncertainty in calculating the liquid potentials.