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OXIDATION-REDUCTION POTENTIALS IN NON-AQUEOUS SOLUTIONS. PART II.

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The present communication is an extension of the work described in Part $I.^1$ to other systems and to other solvents such as acetonitrile, benzonitrile and acetone. These solvents and pyridine are of interest from the point of view of the mechanism of the formation of a potential at an oxidation-reduction electrode since they do not ionise to give hydrogen or hydroxide ions.

One series of measurements has been made in anhydrous acetic acid and although this solvent ionises to give hydrogen ions, the results are nevertheless interesting on account of the investigations of von Hevesy and Zechmeister.² They found from measurements with lead acetate and lead tetra-acetate in acetic acid with the help of a radio-active indicator that an electrolytic oxidation can take place through a direct transfer of charge. Equimolecular amounts of radio-active plumbic acetate and ordinary plumbous acetate (or *vice versa*) were dissolved in acetic acid followed by separation of the two lead salts after a short time. A uniform distribution of lead isotopes between the plumbic and plumbous compounds was found to occur between the molecules and it was concluded that a dynamic equilibrium was set up between the plumbic and plumbous ions according to the scheme:

$$\begin{array}{ll} Pb^{\bullet\bullet\bullet} + Pb^{\bullet\bullet} \rightleftharpoons Pb^{\bullet\bullet\bullet\bullet} + Pb^{\bullet\bullet}. & r.a. \text{ radio-active.} \\ r.a. & r.a. \end{array}$$

If an electrode is present in the system it could participate in the transfer of charges. These authors point out, however, that this is not the only mechanism possible, and that electrolytic oxidations or reductions may take place in some cases through the participation of the solvent.

Experimental.

Preparation of Materials.—(See also Part I.)

Cupric Bromide was prepared by treating A.R. copper with a slight excess of A.R. bromine in the presence of a little water, as recommended

- ¹ Partington and Skeen, Trans. Faraday Soc., 1934, 30, 1062.
- ² Von Hevesy and Zechmeister, Z. Elektrochem., 1920, 26, 151.

by Richards.³ It was kept in a vacuum desiccator over phosphorus pentoxide.

Cuprous Bromide.—A warm dilute solution of cupric bromide, prepared as above, was reduced by sulphur dioxide. The cuprous bromide was kept in the dark in a vacuum desiccator over phosphorus pentoxide.

Cupric Thiocyanate was obtained by taking a moderately concentrated air-free solution of A.R. potassium thiocyanate acidified with a little sulphuric acid and adding immediately the calculated quantity of a concentrated air-free solution of A.R. copper sulphate. The black precipitate was quickly filtered off, washed with a little air-free water, pressed between filter papers and dried in a desiccator over sulphuric acid.

Cuprous Thiocyanate was prepared by reducing a solution containing the appropriate amounts of copper sulphate and potassium thiocyanate with sulphur dioxide.

Lead Tetra-acetate prepared by adding red lead slowly to a mixture of acetic acid and acetic anhydride at 55°-65°, was recrystallised from a mixture of the acid and anhydride, washed with cold acetic acid and dried in a desiccator over sulphuric acid.

Anhydrous Lead Acetate.—A.R. lead acetate was recrystallised three times from conductivity water containing a little acetic acid. The crystals were dehydrated by leaving in a vacuum desiccator over phosphorus pentoxide.

Lithium Acetate.—Pure lithium carbonate was treated with a slight excess of dilute (I:I) acetic acid. The solution when evaporated set to a jelly which crystallised overnight. It was recrystallised twice from redistilled 96 per cent. alcohol, dried at 100°, and kept in a vacuum desiccator over phosphorus pentoxide.

Purification of Solvents.

Pyridine.—In the purification described in Part I., it is advisable to reflux the pyridine with a small quantity of potassium permanganate after the initial fractionation. The pyridine was then distilled and the refluxing with barium oxide followed as usual.⁴ Commercial barium oxide was suitable if the following procedure was adopted. After the initial fractionation the pyridine was refluxed for six hours with a mixture of barium oxide and potassium permanganate. After distillation it was refluxed with a fresh quantity of barium oxide. It was then finally fractionated from a little barium oxide in an atmosphere of dry nitrogen.

The procedure of keeping and using the solvents described in Part I. was adopted. As the solvents were to be used for solutions of substances such as ferrous chloride and cuprous chloride which are easily oxidised, air was prevented from dissolving in the pure solvent and the last fractionation was done in an atmosphere of dry nitrogen.

Acetonitrile was purified by shaking with half its volume of water and then adding solid potassium carbonate until no more dissolved; after separating, the acetonitrile was allowed to stand over a little solid caustic potash for a day, then decanted and allowed to stand over a little solid caustic potash for a week. After distillation it was allowed to stand over a little phosphorus pentoxide for a day. If the first lot of phosphorus pentoxide liquefied it was replaced by some fresh pentoxide until it remained as a lumpy white powder. The liquid was then fractionated in an atmosphere of dry nitrogen with a 12-pear column using the usual precautions to keep out moisture. After standing over some fresh phosphorus pentoxide it was again fractionated in an atmosphere of dry nitrogen and the fraction boiling at 81.5° C. at 760 mm. was collected in the stock bottle. The density found

³ Richards, Proc. Amer. Acad., 1890, **25**, 206; Chem. News, 1891, **63**, 20. ⁴ Mathews and Johnson, J. Physical Chem., 1917, **21**, 294. was $\Delta_{4^{\circ}}^{25^{\circ}} = 0.7767 \pm 0.0001$. The International Critical Tables (Vol. III., p. 28) give $\Delta_{4^{\circ}}^{25^{\circ}} = 0.7770.^{5}$

Benzonitrile was steam distilled and the distillate extracted with ether. The ethereal layer was washed with dilute caustic soda solution and then with dilute sulphuric acid. The product was then allowed to stand over calcium chloride for a few days. After removing the ether on a waterbath it was fractionated under reduced pressure (b.-pt. 120° C. at 10 cm.) using a 25 cm. Hempel column. The middle fraction was left for a day over a little phosphorus pentoxide and then again fractionated under reduced pressure from a little fresh pentoxide. Nitrogen was used to fill the apparatus and also when the pressure was raised. The density found was $\Delta_{4^{\circ}}^{25^{\circ}} = 1.0008 \pm 0.0001$. The value given in the International Critical Tables (Vol. III., p. 28) is $\Delta_{4^{\circ}}^{25^{\circ}} = 1.0005 \pm 0.0003$.

Acetone was dried by means of anhydrous potassium carbonate.6, 7, 8, 9 Acetone (Griffin and Tatlock's A.R.) was allowed to stand over potassium permanganate for 24 hours with occasional shaking. After distillation it was left for a few days with occasional shaking over anhydrous potassium carbonate previously dehydrated at $200^{\circ}-300^{\circ}$ C. for several hours. The acetone was then fractionated using a 75 cm. Hempel column in dry nitrogen, being protected from the atmosphere by calcium chloride and soda-lime tubes. This fractionation from potassium carbonate was carried out two more times, a good deal of the first and last fractions being out two more times, a good deal of the first and last fractions being neglected. The acetone used boiled at 56.3° C. at 760 mm. and had a density of $-\Delta_{4^{2}}^{25^{\circ}} = 0.7847 \pm 0.0001$. Lannung⁸ gives $\Delta_{4^{10}}^{18^{\circ}} = 0.7921$; $\Delta_{4^{\circ}}^{37^{\circ}} = 0.7702$, which give by interpolation $\Delta_{4^{\circ}}^{25^{\circ}} = 0.7841$. The inter-polated value for 20°, namely, $\Delta_{4^{\circ}}^{20^{\circ}} = 0.7898$ agrees fairly well with the value of Bell and co-workers⁶ and Price ¹⁰ who give 0.7908. The refrac-

tive index for sodium light was found to be 1.35715 at 25° C. Acetic Acid was dehydrated by triacetyl borate.¹¹ Triacetyl borate is an excellent dehydrating agent since it reacts with water to yield acetic acid and insoluble boric acid: it was prepared according to the directions of Pictet and Geleznoff.12

A.R. acetic acid (Griffin and Tatlock) was refluxed with the triacetyl borate and then carefully fractionally distilled using a Hempel column : 2 ot 4 times the amount calculated to react with the water present was used. The fraction boiling at 117.9° C. (760 mm.) was collected. Bousfield and Lowry ¹³ give the boiling-point as 117.88° C. \pm 0.05° at 760 mm. and the freezing-point as 16.60° C. \pm 0.005°. Eichelberger and La Mer give the freezing-point as 16.60° C. \pm 0.01° The freezing-point of the product used was 16.59° C. ± 0.01°.

Apparatus and Procedure.

To prevent risk of contamination of the solutions by water, in most cases a reference electrode was used in which the solvent was the same as on the other side of the cell. Thus the reference electrode, Ag | AgCl in pyridine, was used in the case of pyridine solutions. In two cases (solutions in benzonitrile and acetone) suitable reference electrode solutions which could be kept for about 3 or 4 weeks could not be found.

- ¹ Walden and Bill, 2. physical. Chem., 1931, 133, 1.
 ⁸ Lannung, *ibid.*, 1932, 161, 255, 269.
 ⁹ Birr, *ibid.*, 1933, 165, 311.
 ¹⁰ Price, J. Chem. Soc., 1919, 115, 1116.
 ¹¹ Eichelberger and La Mer, J. Amer. Chem. Soc., 1933, 55, 3633.
 ¹² Pictet and Geleznoff, Ber., 1903, 36, 2219.
 ¹³ Bousfield and Lowry, J. Chem. Soc., 1911, 99, 1432.

⁵ Timmermans, Sci. Proc. Roy. Dublin Soc., 1912, 13, 310; and others.

⁶ Bell and co-workers, J. Chem. Soc., 1930, 1927. ⁷ Walden and Birr, Z. physikal. Chem., 1931, **153**, 1.

Here it was necessary to refer the potentials to aqueous solutions and the non-aqueous solutions and the aqueous potassium chloride bridge solution were separated by a ground glass-plug to prevent diffusion. Risk of contamination of the non-aqueous solution by water near the electrode was slight, the taps being kept closed



except during actual measurements (Fig. 3, Cell IIa).

In measurements using acetic acid as solvent, the potentials were referred to the aqueous calomel electrode by a method similar to that described by Conant and coworkers,¹⁴ a saturated solution of lithium acetate in acetic acid being used as bridge solution to separate the aqueous and nonaqueous electrode solutions (Fig. 4, Cell III).

A modification of the cell previously described was used for the pyridine solutions. In this, the connecting tap was reversed (Cell Ia, Fig. 1) in order to facilitate the levelling of the solutions.

In certain cases (where the solvent was acetonitrile) the conductivity of the solutions was good and the two electrode solutions could be separated by a ground-glass plug to prevent diffusion (Cell II, Fig. 2).

All solutions were made up by weight in an atmosphere of dry nitrogen as previously described.

As the solutions used. however, were so dilute that the density did not differ much from that of the pure solvent, the error involved in using the latter figure to calculate the volume of the solution was much less than other experimental errors. The value of the concentration was only necessary in order that a check could be kept on the total concentration of the salts used.

Preparation of the Electrodes.-In a few cells gold as well as platinum electrodes were used. Pieces of gold foil approximately 2 cm. by 1 cm. were suspended by being fused on gold wire. This was fused to platinum wire sealed into glass tubing. Connection was made by silver wire fused to the platinum.



FIG. 2.-Cell II.

The 0.1N-calomel electrode ¹⁵ had a three-way stopcock to enable fresh calomel electrode solution to be run in through the side-arm in place of

¹⁴ Hall and Conant, J. Amer. Chem. Soc., 1927, 49, 3047; Conant and Werner, *ibid.*, 1930, **52**, 4436. ¹⁵ Lewis, Brighton and Sebastian, *ibid.*, 1917, **39**, 2245.

two separate stopcocks. The mercurous chloride was made electrolytically. The cells were first filled with dry nitrogen.



FIG. 3.-Cell IIa.

Cell Ia.—After connecting the right-hand limb and the outlet tube (C) by means of the tap B_{i}

the solution was forced over into the right-hand compartment to the level marked on the outlet tube. The tap was then turned round a little way and the small amount of liquid in C was removed by a roll of filter paper. A slight pressure was then established in the left-hand limb by commencing to force over the other On turning solution. the tap B so as to connect this limb and the outlet tube, the small amount of liquid in the bore of the tap was blown into C and was then removed by filter paper. The left-hand limb was then filled to the same level as the mark on C. The excess liquid in C was



FIG. 4.-Cell III.

then removed by a roll of filter paper. The mark on C was so arranged that by this means the correct amount of solution was run into the electrode vessels. **Cell II.**—The right-hand limb as far as the ground-glass plug (F) was first filled by manipulation of the tap E. The left-hand limb and the middle compartment were filled afterwards. Taps D and E were kept closed except during measurements.

Cell IIa.—Saturated potassium chloride solution was put in the righthand limb as far as the ground-glass plug and filling continued as described above. The intermediate apparatus between the actual cell

and the calomel electrode was used to separate the saturated and $\circ 1N$ potassium chloride solutions.

Cell III .--- The groundglass stopper (G) was placed tightly in position and the saturated potassium chloride solution placed in the intermediate vessel. The solution rose just to the top of the stopper. The nonaqueous bridge solution was then run in through the tap H till it just filled the bore of the tap J. The electrode solution was then run in through the tap K. The tap J was opened only while measurements were being made.

Limits of Accuracy.---Readings were taken to the nearest milliall volt in cases except the systems cupric-cuprous chlorides and cupriccuprous bromides in acetonitrile where they could easily be measured to a tenth of a millivolt, even when using



Results.

Series IV.—Cell Ia used (Table I., Fig. 5). Equilibrium was established almost immediately and the electromotive force remained constant for at least an hour—for eight of the cells it remained constant for about three hours. It then slowly decreased.



FIG. 5.-Series IV.

E.M.F.

0.28

0.26

TABLE I.

+ Pt $\begin{vmatrix} Cu(CNS)_2 \\ in pyridine. \end{vmatrix}$ AgCl in pyridine (0.0244 M.) Ag								
Conc. CuCNS. (Molar).	Conc. Cu(CNS) ₂ (Molar).	Total Conc. (about 0 [.] 023 M.).	Ratio [Cu(CNS)2] [CuCNS]	Log [Cu(CNS)2] [CuCNS]	Per Cent. [Cu(CNS ₂)].	E.M.F. (Volt).		
0.02053 0.02117 0.01886 0.01568 0.01359 0.01213 0.01000 0.00655 0.00489 0.00265 0.00205	0.00108 0.00274 0.00502 0.00654 0.00883 0.01172 0.01438 0.01541 0.01541 0.01815 0.02202 0.02386	0.02161 0.02391 0.02388 0.02222 0.02242 0.02385 0.0242 0.02385 0.02467 0.02304 0.02304 0.02591	0.0524 0.1292 0.2662 0.4176 0.6503 0.9659 1.440 2.355 3.713 8.302 11.66	$\begin{array}{c} -1.281 \\ -0.8887 \\ -0.5748 \\ -0.3792 \\ -0.1869 \\ -0.0151 \\ 0.1584 \\ 0.3720 \\ 0.5698 \\ 0.9192 \\ 1.067 \end{array}$	5.0 11.4 21.0 29.5 39.4 49.1 59.0 70.2 78.8 89.2 92.1	0.136 0.158 0.177 0.189 0.203 0.214 0.222 0.236 0.248 0.268 0.275		

A solution of cupric bromide in pyridine decomposes and the system CuBr₂/CuBr could not be measured.

Series V.-Cell II used (Table II., Fig. 6). An oxidation - reduction system itself was used as a reference (shown on electrode the right) and the solution was stable throughout the whole series of measurements. Equilibrium was established almost immediately; the E.M.F., after remaining constant to within a tenth of a millivolt for about an hour, slowly decreased; it remained constant to within a millivolt for more than 5-6 hours. In the cells in which the





concentration of cupric chloride was over 90 per cent., however, the E.M.F. fell continuously.

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$ \begin{array}{c} \operatorname{Pt} \left \begin{array}{c} \operatorname{CuCl}_2 \\ \text{in acetonitrile.} \end{array} \right \begin{array}{c} \operatorname{CuCl}_2 (0 \cdot 03245 \ M.) \\ \operatorname{CuCl} & \text{in acetonitrile.} \end{array} \right \begin{array}{c} \operatorname{Pt} \\ \operatorname{CuCl} & \operatorname{Othermal}_2 \\ \operatorname{CuCl} & (0 \cdot 03237 \ M.) \end{array} \right $							
Conc. CuCl (Molar).	Conc. CuCl ₂ (Molar).	Total Conc. (about o'o4 M.).	Ratio [CuCl ₂] [CuCl]	Log [CuCl ₂] [CuCl]	Per Cent. [CuCl ₂].	E.M.F. (volt.).	
0.04162 0.03944 0.04319 0.03391 0.03196 0.02639 0.02021 0.01409 0.00808 0.00410 0.00167 0.00017	0.00043 0.00212 0.00527 0.00868 0.01581 0.01786 0.02662 0.02928 0.02928 0.02853 0.03016 0.03198 0.02286	0.04205 0.04156 0.04846 0.04259 0.04777 0.04425 0.04683 0.04337 0.03661 0.03661 0.03426 0.03365 0.02303	0.0102 0.0537 0.1220 0.2560 0.4947 0.6766 1.318 2.077 3.531 7.351 19.16 133.9	$\begin{array}{c} -1.989\\ -1.270\\ -0.9137\\ -0.5919\\ -0.3057\\ -0.1697\\ 0.1198\\ 0.3175\\ 0.5479\\ 0.8664\\ 1.282\\ 2.127\end{array}$	1.0 5.1 10.9 20.4 33.1 40.4 56.9 67.5 77.9 88.0 95.0 99.3	$\begin{array}{c} -0.2285\\ -0.2000\\ -0.1740\\ -0.1435\\ -0.1090\\ -0.0819\\ 0.0921\\ 0.1631\\ 0.2056\\ 0.2445\\ 0.2752\\ 0.2995\end{array}$	

The effect of dilution on a solution in which the concentration ratio was kept constant was measured.

Stock Solution.

+ Pt |**Total Concentration** = 0.06482 M.

Diluted Stock Solution. Total Concentration = 0.04548 M.

Pt - .

E.M.F. = $2 \cdot 7$ millivolts.

Further dilution to about 0.022 M. increased the potential to 0.5 milli-Thus, the effect produced on the electromotive forces of the cells volts. measured by not using solutions of exactly the same total concentration throughout was negligible when compared with differences of potential produced by variation of the concentration ratio.

In a few preliminary measurements an attempt was made to use the reference electrode copper/copper chloride in acetonitrile as in the case of pyridine (Series I). This was discontinued as the green solution of cupric chloride in acetonitrile turned brown in about half an hour in contact with a copper electrode which was also blackened just as in the case of the measurements with pyridine.

Series VI. Cell II used.

CuBr₂ (0·02427 *M*.) in CuBr (0·02426 *M*.) CuBr₂ in acetonitrile. | Pt-. +Ptin acetonitrile. CuBr Reference Electrode.

The results obtained were in all cases smaller than the theoretical E.M.F. but were usually approximately constant for about three hours.

Measurements of this series were also made with the reference electrode CuCl₂

Pt in acetonitrile which was used in the previous series and found CuCl

to be stable.

Series VII. Cell II used.

$$+ \begin{array}{c|c} Pt \\ Au \\ CuBr \\ CuBr \\ CuCl_2 (0.02322M.) \\ in acetonitrile. \\ CuCl_2 (0.02322M.) \\ CuCl (0.02285M.) \\ Reference Electrode. \\ \end{array}$$

Measurements were made with both platinum and gold electrodes but the potentials were not steady. The potential with the gold electrode was initially 0.05 volt more negative than that with the platinum, but this difference fell to 3 to 10 millivolts after about three hours. Addition of a little cupric chloride as a potential mediator had no effect. Changes of colour in the solutions in all cases indicated decomposition.

Series VIII. Cell IIa used.

$$+ Pt \begin{vmatrix} FeCl_3 \\ in benzonitrile. \\ FeCl_2 \end{vmatrix}$$
 Satd. aq. KCl. Aqueous o·1N calomel. Hg. -.

Difficulty was experienced in getting the ferrous chloride to dissolve. Owing to this, and also

to the fact that extremely dilute solutions had to be used, the values obtained were probably not equilibrium values, although in nearly every case the potential remained constant for about an hour.

I.D.CI

The solubility of cupric chloride appeared to be too small to allow measurement of the system CuCl₂/CuCl to be made.

Although both ferric and ferrous chlorides are soluble in acetroni-

trile no measurements could be made with this pair of salts as a solution of the two decomposed within an hour.

Series IX. Cell IIa used (Table III., Fig. 7). Although the solutions were made up just before the cell was filled





they gradually decomposed during the measurement, so that the values given can be regarded as approximate only. Reference electrodes using acetone as solvent :

e.g. Ag/AgCl (s), saturated LiCl in acetone, and $Hg/Hg_2Cl_2 (s)$, saturated LiCl in acetone.

were not used, since (I) solutions of ferric chloride and lithium chloride in acetone react to give an orange precipitate; (2) mercurous chloride in

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+Pt $\begin{vmatrix} FeCl_3 \\ in acetone. \\ FeCl_2 \end{vmatrix}$ Satd. aq. KCl. Aqueous o $\cdot IN$ calomel.								
Conc. FeCl ₂ (Molar).	Conc. FeCl ₃ (Molar).	Total Conc. (about o'o4 M.).	Ratio [FeCl ₃] [FeCl ₂]	Log [FeCl ₃] [FeCl ₂]	Per Cent. [FeCl ₃].	E.M.F. (volt).		
0·03246 0·03067 0·02256 0·01494 0·00402	0-00493 0-01320 0-02032 0-03096 0-03628	0·03739 0·04387 0·04288 0·04590 0·04030	0·1519 0·4302 0·9008 2·073 9·021	0.8185 0.3664 0.0454 0.3167 0.9552	13·2 30·1 47·4 67·5 90·0	0.055 0.200 0.392 0.533 0.788		

TABLE III.

a solution of lithium chloride in acetone reacts to give a grey product; (3) the process of solution in non-aqueous solutions is sometimes slow and



E.M. 1.00 0.95 <u>0.90</u> 🗆 a 0.8 0.80 Ø Log [Pb (CH3 COQ)4] 0.75 [Pb(CH3 C00]2 0.70 0 1.2 0.8 0.6 0.4 0.2 0 0.2 0.4 0.6 0.8 1.0 1.0 1.2 + FIG. 8.-Series X.

so saturation might not always be obtained if fresh solutions were to be made up for each cell.

Series X. Cell III used (Table IV., Fig. 8). The potentials with the platinum electrodes were not very definite : the potential increased rapidly for about one to two hours to the value given, then remained constant for about half an 80 % [Pb(CH3C00)4] hour, and afterwards slowly increased. The potential at the gold

electrode remained practically constant for about two to three hours after only a s m all increase.

Some platinum electrodes gave unreliable results. New platinum foil gave results similar to old pieces which had been used several times.

Electrodes washed in alcohol and heated in a flame nearly always gave

TABLE IV.

$\begin{array}{c c} Pt \\ + \begin{array}{c} Pb(CH_{3}COO)_{4} \\ in \ acetic \ acid. \end{array} & \begin{array}{c} Saturated \\ CH_{3}COOLi \\ in \ acetic \ acid. \end{array} & \begin{array}{c} Satd. \\ aq. \ KCl. \end{array} & \begin{array}{c} Aqueous \\ o \cdot I \\ calomel. \end{array} & Hg - \begin{array}{c} Pb(CH_{3}COO)_{2} \end{array} & \begin{array}{c} Pb(CH_{3}COO)_{4} \\ e - Pb(CH_{3}COO)_{4} \\ e - Pb(CH_{3}COO)_{4} \end{array} & \begin{array}{c} Pb(CH_{3}COO)_{4} \\ e - Pb(CH_{3}COO)_{4} \\ e - Pb(CH_{3}COO)_{4} \end{array} & \begin{array}{c} Pb(CH_{3}COO)_{4} \\ e - Pb(CH_{$									
Conc. Pb(CH ₃ COO) ₂ (Molar).	Conc. Pb(CH ₃ COO) ₄ (Molar).	Total Conc. (about o'o4 <i>M</i> .).	Ratio [Pb(CH ₃ COO) ₄] (Pb(CH ₃ COO) ₂]	Log [Pb(CH ₃ COO),] [Pb(CH ₃ COO),]	Per Cent. [Pb(CH ₃ COO) ₄].	E.M.F. (Platinum).	E.M.F. (Gold).		
0.03713 0.03183 0.03091 0.02638 0.02861 0.02458 0.01838 0.01808 0.01808 0.01164 0.01132 0.00879 0.00546 0.00180	0.00167 0.00413 0.00629 0.00853 0.00949 0.01473 0.01824 0.01797 0.02171 0.02165 0.02697 0.02645 0.03207 0.03495	0.03880 0.03596 0.03720 0.03491 0.03810 0.03931 0.03662 0.03662 0.03662 0.03642 0.03523 0.03523 0.03523 0.03575	0.0449 0.1299 0.2035 0.3233 0.3318 0.5991 0.9920 0.9942 1.476 1.860 2.383 3.010 5.868 19.40	$\begin{array}{c} -1.3477 \\ -0.8863 \\ -0.6915 \\ -0.4904 \\ -0.4792 \\ -0.2225 \\ -0.0035 \\ -0.0025 \\ 0.1692 \\ 0.2696 \\ 0.3772 \\ 0.4786 \\ 0.7685 \\ 1.2877 \end{array}$	4·3 11·5 16·9 24·4 24·9 37·5 49·8 49·9 59·6 65·0 70·4 75·1 85·4 95·1	0.688 0.727 0.755 0.790 0.813 0.835 0.825 0.835 0.845 0.865 0.865 0.880 0.920 0.973	0.874 		

indefinite results. The gold electrode was least affected by washing with alcohol and heating in a flame.

In order to compare some of the results with those of Abegg and Neustadt,¹⁶ in two other cases, namely, the systems $CuCl_2/CuCl$ in acetonitrile and $Cu(CNS)_2/CuCNS$ in pyridine, the potentials were referred to aqueous solutions using the same method as employed in series VIII. and IX. (Cell IIa). The first cell measured was ([CuCl_2]/[CuCl] = 1):

+Pt
$$\begin{vmatrix} \text{CuCl}_2 \\ \text{CuCl} \end{vmatrix}$$
 in acetonitrile. $\begin{vmatrix} \text{Satd. aq.} \\ \text{KCl.} \end{vmatrix}$ Aqueous o $\cdot IN$. calomel. $\begin{vmatrix} \text{Hg}_{-} \\ e_1 \\ e_2 \\ E = e_1 - e_2 + e_3 = 0.565 \text{ volt.} \end{vmatrix}$

Taking $e_2 = 0.333$ (value for 0.1N calomel at 25° C., the liquid junction potential between the saturated and 0.1N potassium chloride solutions being negligibly small) and neglecting the liquid junction potential between the aqueous and non-aqueous solutions, we find :

$$e_{1} = E_{0} + \frac{RT}{F} \log_{e} \frac{[\operatorname{CuCl}_{2}]}{[\operatorname{CuCl}]} = 0.898.$$

$$\therefore E_{0} = 0.898, \text{ since } \log \frac{[\operatorname{CuCl}_{2}]}{[\operatorname{CuCl}]} = 0.$$

This is the value of the normal oxidation-reduction potential of the system $CuCl_2/CuCl$ in acetonitrile if we assume the liquid junction potential is negligible and the ratio of the activities of the cupric and cuprous ions is equal to the ratio of the concentrations of the salts.

The other cell measured $([Cu(CNS)_{1}]/[CuCNS] = 1)$ was :

+Pt
$$\begin{vmatrix} Cu(CNS)_2 \\ in pyridine. \end{vmatrix}$$
 Satd. Aq. KCl. $\begin{vmatrix} Aqueous \ o \cdot I \ N \\ calomel. \end{vmatrix}$ Hg-.

 $E = e_1 - e_2 + e_3 = 0.050.$

Whence

$$E_0 = 0.383.$$

This is close to Abegg and Neustadt's value of 0.37 volt for the system $CuCl_2/CuCl$ in pyridine, although the agreement is fortuitous. Thus, the value of E_0 for the system $CuCl_2/CuCl$ in pyridine, although it has not been measured in the present research, is on the assumptions made above about 0.28 volt, about 0.10 volt less than that of the $Cu(CNS)_2/CuCNS$ system. The reference electrodes in the two series were nearly the same and the electromotive forces of the former were found to be about 0.10 volt less than those of the second system. These various values differ considerably from the value of E_0 for aqueous solutions, namely 0.16 volt.

Abegg and Neustadt's conclusion that the normal oxidation-reduction potential was the same in pyridine as in water does not seem to be correct. Some of the difference may be accounted for by the different degrees of dissociation of the salts in the non-aqueous solutions and also by some error probably made in neglecting the liquid junction potential.

The following approximate solubilities at 25° C. were determined to complete the data on the solubilities of the salts employed.

Pyridine. Cupric thiocyanate, 0.045M. Cuprous thiocyanate contains more than 20 gms. per litre.

Benzonitrile. Anhydrous ferrous chloride, 0.012M.

Acetone. Anhydrous ferrous chloride, 0.147M. Potassium ferricyanide is insoluble.¹⁷

Acetic acid. Lead tetra-acetate, 0.075M. Anhydrous lead acetate, 2.03M. Lithium acetate approximately 1.83M.

Discussion.

The electromotive force of the cell:

Pt | Oxidised form | Reference Electrode,

can be expressed by the equation (Peters' formula):

$$E = E_0' + \frac{RT}{nF} \log_e \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

 E_0' is a constant which includes the potential of the reference electrode, the liquid junction potential (assumed to remain constant), and the normal oxidation-reduction potential of the system. On the assumption that the ratio of the activities of the ions of oxidised and reduced forms is equal to the ratio of the concentrations of oxidised and reduced salts, the logarithm of this ratio (as abcissa) plotted against E (as ordinate) should approximate to a straight line. When the potentials were definite the only exception found was the system CuCl₂/CuCl in acetonitrile.

¹⁷ Cf. Naumann, Ber., 1904, 37, 4328.

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E has also been plotted against the percentage concentration of the oxidised form. When due regard is had to the approximate assumptions involved in the equation, the agreement with similar curves for aqueous solutions is very good, especially in series IV. in which pyridine was the solvent. Series VIII. showed qualitative agreement with the equation, but owing to the small solubility of the ferrous chloride the lower part of the curve was not very definite. The solutions of ferric and ferrous chloride in acetone (Series IX.) were unstable but qualitative agreement with the formula is shown although the differences in the potentials obtained by varying the concentration ratio are much greater than those predicted by theory. Series X. shows good agreement with the oxidation-reduction equation.

The curves obtained with the cupric-cuprous chloride system in acetonitrile (Series V.) are peculiar. Both curves are fairly symmetrical about the point 50 per cent. $[CuCl_2] - 50$ per cent. [CuCl], and the one obtained by plotting E against the percentage concentration of cupric chloride can be considered to be made up of two separate oxidation-reduction curves, one lying between 0 - 50 per cent. $[CuCl_2]$ and the other between 50 - 100 per cent. $[CuCl_2]$. The shape of the curve seems to indicate the formation of a compound (or complex ion) from one molecule (or ion) of cupric chloride and one molecule (or ion) of cuprous chloride is practically colourless or very pale amber, whereas a solution of the two is brown, the colour being deepest when they are present in equimolecular proportions. This compound has been reported to be doubtfully present in various solutions.¹⁸

If this compound exists in the solutions in acetonitrile, there will be oxidation-reduction reactions between it and the simple salts. If the salt present in concentration lower then 50 per cent. combines completely with an equal number of molecules of the salt present in the higher concentration, then in such a solution there will really be the same number of molecules of complex as there were originally of salt in the lower concentration, and the excess of the other salt molecules.

Let the solution contain x per cent. of the oxidised form $(CuCl_2)$ and (100 - x) per cent. of the reduced form (CuCl). Two cases must be considered, viz. (1) (100 - x) > x, and (2) x > (100 - x).

In case (I) the cuprous salt will be in excess. There will be (100 - 2x) per cent. CuCl left, since approximately x per cent. has combined with the x per cent. of CuCl₂ to form x per cent. of complex, and there will be practically no CuCl₂ left. In case (2) practically all the (100 - x) per cent. CuCl will combine sith an equal amount of CuCl₂ to form approximately (100 - x) per cent. of complex, and there will be $\{x - (100 - x)\} = (2x - 100)$ per cent. CuCl₂ left. If the complex ion is assumed to be Cu₂^{**}, the charge difference as compared with Cu₂^{**} and 2Cu^{**} is in each case unity (y = I).

Thus, in the range 0 - 50 per cent. $[CuCl_2]$, we have an oxidationreduction relation between the cuprous salt and the complex, the latter giving the higher valency ion, and in the range 50 - 100 per cent. $[CuCl_2]$ one between the complex and the cupric salt in which the latter now gives the higher valency ion. The normal oxidation-reduction potential of the latter system must be greater than that of the former to give the correct shape of the curve.

¹⁸ Kohlschütter, *ibid.*, 1904, **37**, 1153.

$$E = E_{0} + \frac{RT}{yF} \log_{e} \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$
$$E' = E_{0}' + \frac{RT}{yF} \log_{e} \frac{x}{(100 - 2x)},$$

or

Case (1)

$$E' = a' + b' \log \frac{x}{(100 - 2x)}$$
 where a and b are constants.

Case (2).
$$E'' = a'' + b'' \log \frac{(2x - 100)}{(100 - x)}$$
.

The values of a and b were found by taking two points on the curve (marked by asterisks in the table) and the equation checked with other points. The agreement is fairly good (Table V.).

TABLE V.

$\mathbf{o} - \mathbf{E}' = -\mathbf{o} \cdot \mathbf{I}$	50 per cent. [0 16 + 0·0694 log	$\operatorname{CuCl}_{2}].$ $\frac{x}{(100-2x)}.$	50 - 100 per cent. [CuCl ₂]. $E'' = 0.155 + 0.120 \log \frac{(2x - 100)}{(100 - x)}.$			
z Per Cent.	E.M.F. (Obs.).	E.M.F. (Calcd.).	Per Cent.	E.M.F. (Obs.).	E.M.F. (Calcd.).	
0 10 20 25 30 40	0.179 0.150 0.135 0.125 0.085	∞ -0·179* -0·149 -0·137 -0·125* -0·095	60 70 75 80 90 100	0.119 0.175 0.192 0.212 0.252	0.119* 0.170 0.191 0.212* 0.263 ∞	

The results cannot be easily explained as entirely due to the effect of dilution on the dissociation of the two simple salts.

Thus, at the point 10 per cent. $[CuCl_2]$, let α'_{10} be the degree of dissociation of the CuCl₂ of concentration c'_{10} , and α''_{90} the degree of dissociation of the CuCl of concentration c''_{90} .

sociation of the CuCl of concentration c''_{90} . Similarly at the point 90 per cent. [CuCl₂], let α'_{90} be the degree of dissociation of the CuCl₂ of concentration c'_{90} , and α''_{10} the degree of dissociation of the CuCl of concentration c'_{10} .

Then
$$E_{10} = -0.179 = E'_0 + \frac{RT}{F} \log_e \frac{\alpha'_{10} \cdot c'_{10}}{\alpha''_{90} \cdot c''_{90}}$$

and

Whence

$$E_{90} = 0.252 = E'_{0} + \frac{RT}{F} \log_{e} \frac{\alpha'_{90} \cdot c'_{90}}{\alpha''_{10} \cdot c''_{10}}$$
$$\frac{\alpha'_{90}}{\alpha''_{10}} / \frac{\alpha'_{10}}{\alpha''_{90}} = 2.41 \times 10^{5}$$

Suppose on dilution from 90 per cent. to 10 per cent. $(c'_{90} - c'_{10})$ the degree of dissociation of the CuCl₂ $(\alpha'_{90} - \alpha'_{10})$ is affected to approximately the same extent as that of the CuCl $(\alpha''_{90} - \alpha''_{10})$ on dilution from 90 per cent. to 10 per cent. $(c''_{90} - c''_{10})$, then the above ratio indicates that *dilution* of the CuCl₂ and also of the CuCl approximately 9 times over similar concentration ranges would *decrease* the degree of dissociation of each by approximately 500 times.

Summary.

Peters' formula can be applied quantitatively to several oxidationreduction systems in stable non-aqueous solutions : in a few cases unknown complex formation may occur giving potentials which do not agree directly with the equation but are definite, reproducible, and appear to follow a modified form of the equation. In certain cases indefinite potentials are given at unattackable electrodes.

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