

vapor only. The liquid meniscus in the capillary tube appeared to be truly hemispherical under high magnification, with a solid-liquid contact angle of zero. The capillary heights were measured with a Gaertner cathetometer which could be read directly to 0.0001 cm. The light which illuminated the reference surface was directed through a narrow horizontal slit cut into a brass plate which was vertically adjustable. With the aid of this apparatus the reference surface was thrown in sharp silhouette and its position readily determined. Thirty minutes was allowed at each temperature for the capillarimeter contents to reach thermal equilibrium with the water-bath. Between readings, the liquid was made to flow the full length of the capillary by tipping the apparatus nearly horizontal. When the vertical position was resumed, the liquid flowed spontaneously to its equilibrium position with a receding contact angle. Each recorded measurement was the average of from 20 to 30 readings made on different days.

Results

The data were applied in the following form of the capillary-height equation

$$\gamma = \frac{r \left(h + \frac{r}{3} \right) (d_l - d_v) g}{2}$$

where r is the radius of the capillary, h the observed capillary height, d_l and d_v the density of the liquid and vapor, respectively, and g the gravitational factor. Although the vapor densities have been accurately measured in this Laboratory, it was

found that they were not significant over the temperature range employed, and accordingly were not used in the density correction. The densities and surface tension values for seven temperatures are shown in Table I. The following equations, which

TABLE I

THE DENSITY AND SURFACE TENSION OF MOLTEN MONOFLUOROACETIC ACID

Temp., °C.	Density of molten compd. g./cc.	Surface tension, dynes/cm.
36	1.3693	38.21 ± 0.05
40	1.3639	37.76
50	1.3505	36.65
60	1.3372	35.54
70	1.3238	34.43
80	1.3105	33.32
95	1.2905	31.64 ± 0.05

relate the density and the surface tension, respectively, to the temperature, were formulated by the method of least squares.

$$d = 1.4173 - 0.00133t$$

$$\gamma = 42.220 - 0.11145t$$

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COMMUNICATIONS TO THE EDITOR

DICHLORO-BIS-(2,2'-DIPYRIDYL)-IRON(II) AND DICHLORO-BIS-(1,10-PHENANTHROLINE)-IRON (II)

Sir:

Calvin and Melchior¹ point out that there is a correlation between the stability of complexes of bivalent metal ions and the second ionization potentials of the gaseous metal atoms. This was also reported independently by Irving and Williams.² In a recent detailed treatment of this subject they³ suggest this stability order follows from considerations of the reciprocal of the ionic radii and the second ionization potentials.

It is well known that salts of the hydrated iron(II) ion are paramagnetic with "ionic" or sp^3d^2 bonds, whereas salts of $[Fe(dipy)_3]^{+2}$ and $[Fe(o phen)_3]^{+2}$ are diamagnetic,⁴ indicative of strong covalent d^2sp^3 hybridization. In the stability sequence of complexes of bivalent metals these iron(II) complexes are anomalously high,³ and furthermore the values of K_3 for the stepwise formation constants⁵ in contrast to the usual trend, are

(1) M. Calvin and N. C. Melchior, *THIS JOURNAL*, **70**, 3270 (1948); first reported in N. C. Melchior, Thesis, University of California, Berkeley, September, 1946.

(2) H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

(3) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

(4) L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **63**, 767 (1933); **64**, 772 (1935); F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(5) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *THIS JOURNAL*, **70**, 2348 (1948); J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

greater than K_1 or K_2 . Irving and Williams³ have proposed that these anomalies arise from orbital stabilization, and it is thus of particular interest to determine whether diamagnetism is associated with the addition of the first, second or third chelate molecule.

When solid $[Fe(dipy)_3]Cl_2 \cdot 6H_2O$ was heated in an Abderhalden pistol at 100° over concentrated sulfuric acid *in vacuo* for thirty hours loss of the water and one molecule of 2,2'-dipyridyl resulted.

Anal. Calcd. for $C_{20}H_{16}N_4FeCl_2$: C, 54.70; H, 3.65. Found: C, 54.49; H, 3.80.

At 156°, $[Fe(o phen)_3]Cl_2 \cdot 6H_2O$ also lost the water and one molecule of the base becoming blue.

Anal. Calcd. for $C_{24}H_{16}N_4FeCl_2$: C, 59.16; H, 3.28. Found: C, 58.66; H, 3.22.

On further heating at 156° *in vacuo* $[Fe(dipy)_2Cl_2]$ lost an additional molecule of 2,2'-dipyridyl changing from violet-blue to red.

Anal. Calcd. for $C_{10}H_8N_2FeCl_2$: C, 42.44; H, 2.83; N, 9.90. Found: C, 42.75; H, 2.94; N, 10.14.

At 197° *in vacuo* $[Fe(o phen)_2Cl_2]$ was unchanged after several hours.

Magnetic susceptibilities were determined by the Gouy method. A value of 5.2 B.M. was obtained for $[Fe(dipy)_2Cl_2]$ and 5.3 B.M. for $[Fe(o phen)_2Cl_2]$ in agreement with the theoretical value for four unpaired electrons and indicative of "ionic" or sp^3d^2 bonding. These results lend ex-

perimental support to the postulate of orbital stabilization.⁴ The susceptibility of the *mono* compound, 1.8 B.M., corresponds to one unpaired electron. This is not consistent with the theoretical values expected from the simple formula [Fedipy-Cl₂] and may suggest a certain amount of metal-metal interaction. Detailed studies on these and similar compounds will be published later.

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RECEIVED JANUARY 13, 1954

THE OXYGEN-HYDROGEN PEROXIDE COUPLE AT THE DROPPING MERCURY ELECTRODE

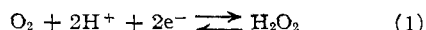
Sir:

The first oxygen wave of the dropping mercury electrode (D.M.E.) arises from the two electron reduction of oxygen to hydrogen peroxide. Although this wave has universally been considered highly irreversible,¹ it was recently reported² that in unbuffered basic solutions hydrogen peroxide yields an anodic wave at the same potential. From this and other observations the investigators concluded that the oxygen-hydrogen peroxide reaction is completely reversible, but involves only one electron.

These conclusions are not consonant with the fact that H₂O₂ (or HO₂⁻) and O₂ must be the diffusing species, and hence two electrons be involved in the over-all electrode process; and they conflict with the insensitivity of the oxygen half-wave potential ($E_{1/2}$) to changes in *p*H, as reported by Kolthoff and Miller.³ In view of the fundamental importance of the oxygen wave in polarography, it was considered important to resolve this problem, and a preliminary report is provided in this Communication.

Polarograms of oxygen, hydrogen peroxide and their mixtures were run in buffered solutions, *p*H range 7.5-13, of ionic strength 0.15. In all these solutions, anodic and cathodic waves were observed, which in the less basic media exhibited the usual criteria of irreversibility—drawn-out shapes, non-linear "log plots," and in the case of the oxygen wave an $E_{1/2}$ which hardly varied with *p*H. In mixtures of hydrogen peroxide and oxygen the two waves joined without inflection; however, the $E_{1/2}$ shifted as the composition of the mixture was varied. This irreversible nature diminished as the alkalinity increased, until at *p*H 12 both anodic and cathodic waves gave identical $E_{1/2}$'s, and the log plot of both had the theoretical slope for a two-electron reaction.

At the point at which the electrolysis current in a H₂O₂-O₂ mixture crosses the residual current, the D.M.E. is functioning as a potentiometric null point detector. The "crossing point" potential will depend upon the bulk concentration as predicted by the Nernst equation, provided that we are dealing with the over-all reaction



(1) Kolthoff and Lingane, "Polarography," 2nd edition, Vol. II, Interscience Publishers, Inc., New York, N. Y., p. 552.

(2) S. Hacobian, *Australian Journal of Chemistry*, **6**, 211 (1953).

(3) I. M. Kolthoff and C. S. Miller, *This Journal*, **68**, 1013 (1941).

for which the Nernst equation at 25° is

$$E = E^0 + 0.0296 \log (\text{O}_2)/(\text{H}_2\text{O}_2) - 0.0592 \text{pH} \quad (2)$$

Supposing that the absolute rate theory as recently applied to polarographic phenomena⁴ is applicable here, it can be shown that these equations apply at the crossing point, however irreversible the waves may be.

In fact, Equation (2) was found to hold very well both with regard to the *p*H and the O₂-H₂O₂ ratio (corrected for the acid dissociation of H₂O₂) over the entire range investigated. The value $E^0 = +0.70 \text{ v.} \pm 0.01 \text{ v.}$ was found for the standard potential of the half-cell of Equation (1), in good agreement with Latimer's calculated value +0.682 v.⁵

These experimental results are also in good accord with the observations of Berl,⁶ who found that the O₂-H₂O₂ couple was reversible at graphite and activated carbon electrodes in solutions of *p*H between 13 and 15, with an E^0 of +0.684 v.

In the range of *p*H studied the O₂-H₂O₂ couple at the D.M.E. evidently is of the transition (semi-reversible) type.⁷ The situation is complicated by the probable presence of two steps⁸ which may differ in degree of reversibility and dependence on *p*H. Analysis of the irreversible nature of the waves is continuing with the hope of elucidating the mechanism and kinetics of oxygen reduction. The combined results will be presented in a future publication.

(4) Tanford and Wawzonek, "Annual Reviews of Physical Chemistry," **3**, 247 (1952).

(5) W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., p. 43.

(6) W. G. Berl, *J. Electrochem. Soc.*, **83**, 253 (1943).

(7) P. Delahay, *This Journal*, **75**, 1430 (1953); M. Smutek, *Coll. Czech. Chem. Comm.*, **18**, 171 (1953).

(8) One of these may be the reversible one-electron step postulated by Hacobian, see ref. 2.

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9 α -FLUORO DERIVATIVES OF CORTISONE AND HYDROCORTISONE

Sir:

In a recent communication¹ we have described a new group of derivatives of cortisone and hydrocortisone, in which the 9 α -hydrogen atom is replaced by halogen. The main interest in this series of compounds derived from the fact that they possessed marked glucocorticoid activity, which in the case of the chloro derivatives exceeded by a factor of 4 that of the parent hormones. The finding that the activity was inversely proportional to the size of the halogen atom prompted the preparation of the last remaining members of this group, the 9 α -fluoro derivatives, the description of which is the purpose of this communication.

9 α -Fluorohydrocortisone acetate (I), m.p. 233-234°; $[\alpha]_D^{25} +123^\circ$ (*c*, 0.64 in CHCl₃); $\lambda_{\text{max}}^{\text{alc.}}$ 238 μ ($\epsilon = 16,800$); $\lambda_{\text{max}}^{\text{Nujol}}$ 2.94 μ , 3.03 μ (OH), 5.75 μ , 5.82 μ (acetylated side chain), 6.07 μ , 6.11 μ

(1) J. Fried and E. F. Sabo, *This Journal*, **75**, 2273 (1953).

(2) Occasionally samples began to melt at 205-208°, resolidified and eventually melted at 226-228°, probably due to polymorphism.