After dialyzing out the urea from several of the most concentrated solutions, the rotatory dispersion constant returned to its original value at 0.5°, showing that gelatin had undergone no denaturation by urea.

GENEVA, NEW YORK

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[CONTRIBUTION FROM THE PHYSICS LABORATORIES, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

# Magneto-Optic Rotations of Paramagnetic Ions

BY SAMUEL STEINGISER AND HERBERT HYMAN

The purpose of this investigation was to observe the magneto-optic rotations of dilute solutions of complex iron salts, and to determine the partial Verdet constants. The three salts investigated were potassium ferricyanide, potassium ferrocyanide, and ferric ammonium sulfate. Ferrous ammonium sulfate was also tried, but since it absorbed most of the light in the range of the sodium lamp, accurate measurements could not be made.

## Experimental

**Materials and Apparatus.**—All chemicals were of C. P. grade. Since, in the very dilute solutions used, a relatively large impurity would be necessary to affect the results, no further purification was attempted. The concentrations of the solutions were determined by density measurements. These were made on a chainomatic specific gravity balance, and the concentrations found from tables in the "International Critical Tables."

The source of light, for the values reported, was a General Electric Sodium Lab-Arc, $\lambda_D = 5893$ Å. (Earlier preliminary investigations were made using a mercury vapor quartz arc, but this was abandoned in favor of the more universal sodium arc.) Nicol prisms were used as polarizer and analyzer. The angle setting on the scale could be read to 0.1° and estimated to within 0.01° with the aid of a telescope and cross-hair. The Pyrex glass cell, containing the liquid under investigation, was a 21.6-cm. long tube with the ends of optically flat glass fused into the body of the cell. No cement was used on any part of the tube. It was mounted on wooden supports inside the hollow core of a large coil. The coil was 25 cm. in length, formed by winding 2-mm. diameter insulated copper wire in 17 layers of 125 turns each on a copper cylinder. The coil extended sufficiently beyond the tube to eliminate any distortion of the magnetic field due to edge effects.

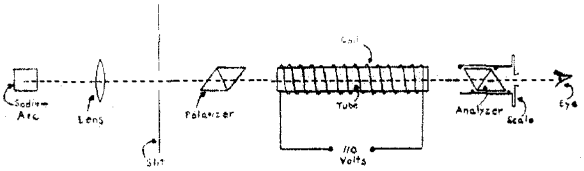

Fig. 1.—Schematic diagram of apparatus.

The apparatus was calibrated using carbon disulfide and distilled water over a range of currents as can be seen from the data. The Verdet constants for these two liquids were obtained from the "International Critical Tables." In order to facilitate calculations of the Verdet constants of the solutions under investigation, a conversion factor was found, as shown, equal to 0.0399 Verdet unit/deg./amp.

**Measurements.**—The values reported are the average of nine independent measurements with the field off, recorded in the tables below as $N^0$, nine with the field causing rotation clockwise, $R^0$, and finally nine with the field causing rotation counterclockwise, $L^0$. Altogether twenty-seven readings were taken for each solution and the average with its mean deviation calculated.

Although the partial Verdet rotations of some of the salts are in opposite directions to that of water, the actual rotations, in all cases measured, were in the same direction, due to the rather dilute solutions used. The partial Verdet constant is defined so that

$$N_1V_1 + N_2V_2 = V$$

where $N_2$ and $N_1$ are the mole fractions of the solute and solvent, respectively, $V$ is the observed Verdet constant for the solution, and $V_2$ and $V_1$ are the partial Verdet constants of the solute and solvent. This equation is by definition exact, but in using it to determine $V_2$, it is necessary to make the assumption that $V_1$ equals the Verdet constant of pure water. While this undoubtedly is not true in concentrated solutions, it is probably true within the limit of experimental error in the solutions used in these measurements. $V_2$ is not necessarily the Verdet constant of the pure salt and should not be regarded as such, but is the Verdet constant of the salt in the solution of definite molality. There is considerable evidence to show that it may be regarded as constant over a considerable range of concentrations.

The agreement between the two standardizing substances is thus seen to be very good.

The factor for converting the rotation deg./amp. into Verdet units is 0.0399 Verdet unit/deg./amp.

### CALIBRATION DATA

Distilled water $V = 0.01306$ min./cm. oersted at 30°C.

| No. | Current $I$, amp. | $N^0$ | Reading in deg. $R^0$ | $L^0$ | Rotation in deg. $N^0 - R^0$ | $N^0 - L^0$ | $\frac{1}{2}(R^0 - L^0)$ | Rotation/unit current $N^0 - R^0/I$ | $N^0 - L^0/I$ | $R^0 - L^0/2I$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 14.7 | 49.78 | 45.05 | 54.70 | 4.73 | 4.92 | 4.84 | 0.322 | 0.335 | 0.329 |
| 2 | 14.6 | 49.52 | 45.05 | 54.45 | 4.47 | 4.93 | 4.70 | .311 | .338 | .322 |
| 3 | 14.5 | 49.82 | 44.64 | 54.60 | 5.18 | 4.58 | 4.88 | .358 | .317 | .337 |
| 4 | 14.3 | 49.65 | 44.95 | 54.29 | 4.70 | 4.64 | 4.67 | .328 | .323 | .326 |
| 5 | 14.4 | 49.80 | 44.95 | 54.50 | 4.85 | 4.70 | 4.78 | .336 | .326 | .332 |
| 6 | 14.3 | 49.45 | 45.00 | 54.10 | 4.45 | 4.55 | 4.50 | .311 | .318 | .315 |
| 7 | 14.3 | 49.65 | 44.76 | 54.45 | 4.89 | 4.80 | 4.84 | .343 | .337 | .328 |
| 8 | 14.4 | 49.63 | 45.30 | 54.42 | 4.33 | 4.79 | 4.56 | .301 | .333 | .317 |
| 9 | 14.3 | 49.68 | 45.05 | 54.44 | 4.63 | 4.81 | 4.72 | .324 | .336 | .329 |
| | | | | | | | Mean | .326 | .329 | .327 |
| | | | | | | | | ±.004 | ±.002 | ±.002 |

Rotation, degrees/amp. = 0.327 ± 0.002.
0.01306/0.327 = 0.0399 Verdet unit/deg./amp.

Carbon disulfide $V = 0.04151$ at 30°

| No. | Current $I$, amp. | $N^0$ | Reading in deg. $R^0$ | $L^0$ | Rotation in deg. $N^0 - R^0$ | $N^0 - L^0$ | $\frac{1}{2}(R^0 - L^0)$ | Rotation/unit current $N^0 - R^0/I$ | $N^0 - L^0/I$ | $R^0 - L^0/2I$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 14.7 | 82.55 | 67.40 | 98.20 | 15.15 | 15.65 | 15.40 | 1.031 | 1.065 | 1.048 |
| 2 | 14.5 | 82.85 | 67.70 | 98.40 | 15.15 | 15.55 | 15.35 | 1.044 | 1.071 | 1.059 |
| 3 | 14.4 | 82.72 | 67.21 | 98.15 | 15.51 | 15.43 | 15.47 | 1.078 | 1.071 | 1.074 |
| 4 | 14.1 | 82.87 | 67.80 | 98.17 | 15.07 | 15.30 | 15.18 | 1.068 | 1.082 | 1.076 |
| 5 | 10.8 | 83.19 | 71.80 | 93.60 | 11.39 | 10.41 | 10.90 | 1.051 | 0.964 | 1.008 |
| 6 | 10.8 | 82.89 | 71.60 | 93.80 | 11.29 | 10.91 | 11.10 | 1.041 | 1.009 | 1.027 |
| 7 | 10.6 | 82.70 | 71.80 | 93.50 | 10.90 | 10.80 | 10.85 | 1.028 | 1.019 | 1.022 |
| 8 | 10.6 | 83.21 | 72.06 | 93.56 | 11.15 | 10.35 | 10.75 | 1.051 | 0.976 | 1.014 |
| 9 | 8.4 | 82.82 | 74.01 | 92.00 | 8.81 | 9.18 | 8.99 | 1.050 | 1.091 | 1.071 |
| 10 | 8.5 | 82.76 | 73.62 | 91.96 | 9.14 | 9.20 | 9.17 | 1.075 | 1.085 | 1.080 |
| 11 | 7.2 | 82.39 | 74.65 | 89.78 | 7.74 | 7.39 | 7.56 | 1.074 | 0.998 | 1.021 |
| 12 | 7.2 | 82.71 | 74.80 | 89.80 | 7.91 | 7.09 | 7.50 | 1.098 | .984 | 1.042 |
| 13 | 5.9 | 82.90 | 76.64 | 89.00 | 6.26 | 6.10 | 6.18 | 1.061 | 1.032 | 1.044 |
| 14 | 5.9 | 82.41 | 76.25 | 88.38 | 6.16 | 5.97 | 6.07 | 1.042 | 1.012 | 1.028 |
| 15 | 5.9 | 82.90 | 76.40 | 88.81 | 6.50 | 5.91 | 6.21 | 1.099 | 1.002 | 1.050 |
| 16 | 6.0 | 83.05 | 76.18 | 88.75 | 6.87 | 5.70 | 6.28 | 1.160 | 0.950 | 1.045 |
| | | | | | | | Mean | 1.063 | 1.026 | 1.044 |
| | | | | | | | | | | ±.004 |

Rotation, degrees/amp. = 1.044 ± 0.004.
0.04151/1.044 = 0.0398 Verdet unit/deg./amp.

### FERRIC AMMONIUM SULFATE, $d^{26}_4$ 1.0105

| No. | Current $I$, amp. | $N^0$ | Reading in deg. $R^0$ | $L^0$ | Rotation in deg. $N^0 - R^0$ | $N^0 - L^0$ | $\frac{1}{2}(R^0 - L^0)$ | Rotation/unit current $N^0 - R^0/I$ | $N^0 - L^0/I$ | $R^0 - L^0/2I$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 13.3 | 52.28 | 48.37 | 56.81 | 3.91 | 4.53 | 4.22 | 0.294 | 0.341 | 0.317 |
| 2 | 13.3 | 52.15 | 48.12 | 56.42 | 4.03 | 4.27 | 4.15 | .305 | .322 | .313 |
| 3 | 13.3 | 52.28 | 48.00 | 56.36 | 4.28 | 4.08 | 4.18 | .321 | .307 | .314 |
| 4 | 13.3 | 52.24 | 48.22 | 56.38 | 4.02 | 4.14 | 4.08 | .304 | .312 | .308 |
| 5 | 13.3 | 52.40 | 48.23 | 56.41 | 4.17 | 3.99 | 4.09 | .315 | .301 | .309 |
| 6 | 13.3 | 52.10 | 47.98 | 56.58 | 4.12 | 4.48 | 4.30 | .310 | .336 | .323 |
| 7 | 13.3 | 52.15 | 48.05 | 56.41 | 4.10 | 4.26 | 4.18 | .309 | .322 | .316 |
| 8 | 13.2 | 52.18 | 48.48 | 56.39 | 3.70 | 4.21 | 3.96 | .281 | .318 | .300 |
| 9 | 13.3 | 52.41 | 47.95 | 56.66 | 4.46 | 4.25 | 4.35 | .337 | .321 | .328 |
| | | | | | | | Mean | .308 | .320 | .314 |
| | | | | | | | | ±.003 | ±.003 | ±.002 |

Molality = 0.0282, mole fraction $N_2$ = 0.000508, $V = 0.314 \times 0.0399 = 0.01253$ Verdet unit, $V_2$ (calcd.) = −1.024 Verdet units.

### POTASSIUM FERRICYANIDE, $d^{26}_4$ 1.0339

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 14.8 | 81.87 | 79.66 | 84.04 | 2.21 | 2.17 | 2.19 | 0.149 | 0.147 | 0.148 |
| 2 | 14.7 | 81.90 | 79.30 | 83.80 | 2.60 | 1.90 | 2.25 | .177 | .129 | .153 |
| 3 | 14.5 | 81.75 | 80.10 | 83.81 | 1.65 | 2.06 | 1.91 | .114 | .123 | .132 |

POTASSIUM FERRICYANIDE $d^{25}_{4}$ 1.0339 (*Concluded*)

| No. | Current $I$, amp. | Reading in deg. | | | Rotation in deg. | | | Rotation/unit current | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $N^0$ | $R^0$ | $L^0$ | $N^0 - R^0$ | $N^0 - L^0$ | $1/2(R^0 - L^0)$ | $N^0 - R^0/I$ | $N^0 - L^0/I$ | $R^0 - L^0/2I$ |
| 4 | 14.6 | 81.90 | 79.84 | 83.90 | 2.06 | 2.00 | 2.03 | 0.141 | 0.140 | 0.139 |
| 5 | 14.4 | 81.78 | 80.24 | 84.20 | 1.54 | 2.42 | 1.98 | .107 | .169 | .138 |
| 6 | 14.5 | 81.65 | 79.10 | 83.54 | 2.75 | 1.69 | 2.22 | .189 | .113 | .153 |
| 7 | 14.4 | 82.00 | 80.20 | 84.40 | 1.80 | 2.40 | 2.10 | .125 | .167 | .146 |
| 8 | 14.4 | 81.80 | 79.70 | 84.02 | 2.10 | 2.22 | 2.16 | .146 | .154 | .150 |
| 9 | 14.2 | 81.64 | 79.80 | 83.45 | 1.84 | 1.81 | 1.83 | .130 | .128 | .129 |
| | | | | | | | Mean | .142 | .144 | .143 |
| | | | | | | | | ±.007 | ±.005 | ±.003 |

Molality = 0.173, mole fraction $N_2$ = 0.00312, $V = 0.143 \times 0.0399 = 0.00571$ Verdet unit, $V_2$ (calcd.) = −2.354 Verdet units.

POTASSIUM FERROCYANIDE, $d^{25}_{4}$ 1.1124

| No. | Current $I$, amp. | $N^0$ | $R^0$ | $L^0$ | $N^0 - R^0$ | $N^0 - L^0$ | $1/2(R^0 - L^0)$ | $N^0 - R^0/I$ | $N^0 - L^0/I$ | $R^0 - L^0/2I$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 14.8 | 52.39 | 47.20 | 57.35 | 5.19 | 4.96 | 5.08 | 0.350 | 0.336 | 0.344 |
| 2 | 14.9 | 52.46 | 47.18 | 57.60 | 5.28 | 5.14 | 5.21 | .354 | .345 | .351 |
| 3 | 14.8 | 52.44 | 47.50 | 57.60 | 4.94 | 5.16 | 5.05 | .334 | .349 | .341 |
| 4 | 14.5 | 52.80 | 47.25 | 57.80 | 5.55 | 5.00 | 5.27 | .383 | .345 | .363 |
| 5 | 14.5 | 52.55 | 47.25 | 58.05 | 5.30 | 5.50 | 5.40 | .365 | .379 | .372 |
| 6 | 14.4 | 82.38 | 77.10 | 87.38 | 5.28 | 5.00 | 5.14 | .367 | .347 | .357 |
| 7 | 14.4 | 82.35 | 77.16 | 87.57 | 5.19 | 5.22 | 5.20 | .360 | .362 | .361 |
| 8 | 14.4 | 82.42 | 77.18 | 87.22 | 5.24 | 4.80 | 5.02 | .363 | .334 | .351 |
| 9 | 14.3 | 83.70 | 78.50 | 88.25 | 5.20 | 4.55 | 4.87 | .363 | .320 | .341 |
| | | | | | | | Mean | .360 | .347 | .353 |
| | | | | | | | | ±.003 | ±.004 | ±.003 |

Molality = 0.415, mole fraction $N_2$ = 0.00748, $V = 0.353 \times 0.0399 = 0.01409$ Verdet unit, $V_2$ (calcd.) = 0.148 Verdet unit.

## Discussion

Welo and Baudisch[1] have shown that, with complex ions having a central atom of a transition element, the paramagnetism can be determined from the effective atomic number. When this has the same value as an inert gas, the complex is diamagnetic, while if it differs from this by *n* units, the complex has a magnetic moment of *n* Bohr magnetons. Thus the six-covalent ferricyanides, as $K_3[Fe(CN)_6]$ with an e. a. n. 26 + 6 + 3 = 35, give *p* (Weiss) = 10, and *b* (Bohr) = *ca.* 1, while the ferrocyanides as $K_4[Fe(CN)_6]$ (e. a. n. 26 + 6 + 4 = 36, the atomic number of krypton) are diamagnetic. Ferric ammonium sulfate probably exists in solution as hydrated $Fe^{+++}$ ion, which is found to be paramagnetic also.

Thus we see that potassium ferricyanide and ferric ammonium sulfate are paramagnetic and also have large negative partial Verdet constants, while potassium ferrocyanide, being diamagnetic, has a relatively low positive partial Verdet constant. There seems to be some correlation between these facts. Scherer and Cordonnier[2,3] have shown that paramagnetic cobalt ions exhibit similar negative Verdet constants over a range of temperatures and wave lengths. Since an error of even 1% in the actual rotation introduces an error of more than 20% in the determination of partial Verdet constants, a quantitative correlation is not possible as yet, but this work has shown a definite connection which may be of use in the future.

Acknowledgment and particular thanks are due to Professors Marcus and Sonkin, of the Physics Department of The City College, for their invaluable aid in this research.

## Summary

The partial Verdet constants of ferric ammonium sulfate, potassium ferricyanide and potassium ferrocyanide were determined and found to be equal to −1.024, −2.354 and +0.148, at molalities 0.0282, 0.173 and 0.415, respectively. The total Verdet constant for each of these molalities was found to be 0.01253, 0.00571 and 0.01409, respectively. The diamagnetic salt, potassium ferrocyanide, shows a normal rotation, while the other salts show a large negative rotation, due to paramagnetism.

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(1) Welo and Baudisch, *Nature*, **116**, 606 (1925).

(2) Scherer and Cordonnier, *Compt. rend.*, **196**, 1724 (1933).

(3) Cordonnier, *ibid.*, **205**, 313 (1937).