$H_2S_2O_7/(IO)_2SO_4$ = 1.8. The formation of un-ionized $IO \cdot HS_2O_7$ would lead to a decrease in the conductivity to a minimum value at the mole ratio $H_2S_2O_7/(IO)_2SO_4$ = 2.0. The observed conductivity minimum occurs, however, at a mole ratio of 1.1 to 1.2, and the conductivity then increases again indicating that conducting species are present at the mole ratio 2.0. We conclude therefore that our results are not in agreement with the formation of either ionized or un-ionized $IO \cdot HS_2O_7$ according to eq. 18.

## Experimental

Experimental details concerning the cryoscopic and conductometric measurements were described in part I.[10] Iodosyl sulfate was prepared by the method of Masson and Argument.[4] Ten grams of finely powdered iodine pentoxide and 5.1 g. of iodine were stirred magnetically under 97% $H_2SO_4$ for 2–3 days. The yellow product was filtered off in a drybox and was washed three times with small portions of 97% $H_2SO_4$ and three times with anhydrous nitromethane. The product was freed from nitromethane by warming gently under vacuum for several hours. It was analyzed by refluxing with water and then extracting the resulting iodine with carbon tetrachloride.

$$5(IO)_2SO_4 + 8H_2O = 6HIO_3 + 2I_2 + 5H_2SO_4$$

The iodine in the $CCl_4$ layer was determined with thiosulfate. Excess KI was added to the acidified aqueous layer and the resulting iodine was titrated with thiosulfate. The results of a typical analysis follow. *Anal.* Calcd.: I, 66.4; oxidation no. of I, 3.00. Found: I, 66.9, 66.8; oxidation no. of I, 2.99, 3.04.

Iodine dioxide was prepared by the method of Bahl and Partington.[8] About 20 g. of finely powdered iodic acid was heated with 70 g. of 97% $H_2SO_4$ for about 40 min. until it had all dissolved. After the solution had been kept in a desiccator for 1 week the yellow solid crust which formed was removed and transferred to a porous plate. This was stored in a desiccator for another week, during which time it was periodically removed and ground to a fine powder. The resulting product was washed with water until the washings were free from sulfate, with acetone until the washings were colorless, and finally with dry ether. The method of analysis was the same as for iodosyl sulfate. *Anal.* Calcd.: I, 79.9; oxidation no. of I, 4.00. Found: I, 78.3, 78.5; oxidation no. of I, 3.99, 4.01.

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# The Kinetics of the Electron Exchange between the 12-Tungstocobaltate(II) and the 12-Tungstocobaltate(III) Anions in Aqueous Solution[1]

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The kinetics of the electron exchange between the 12-tungstocobaltate(II) and 12-tungstocobaltate(III) anions has been studied at 0° in aqueous solution. Precipitation of the $[Co^{III}O_4W_{12}O_{36}]^{-5}$ with $(C_4H_9)_4NI$ was used for separation. The reaction is first order in each ion, and the effects on the rate of changes in the hydrogen ion concentration, ionic strength, temperature, cations, and dielectric constant are described. At 0° and ionic strength of 0.6 $M$ (adjusted with LiCl) the rate constant is 0.63 ± 0.016 $M^{-1}$ sec.$^{-1}$. An "outer-sphere" mechanism is postulated for the system and the results are compared with the theoretical predictions of Marcus.

The preparation and properties of several heteropolytungstate compounds of cobalt have been reported,[3,4] and these compounds have been shown to participate in an unusual sequence of oxidation–reduction reactions.

The oxidation–reduction pair of the 12-tungstocobaltate(II), $[Co^{II}O_4W_{12}O_{36}]^{-6}$, and the 12-tungstocobaltate(III), $[Co^{III}O_4W_{12}O_{36}]^{-5}$, ions, hereafter designated as anions I and II, respectively, particularly interested us, and a quantitative study of the exchange reaction between them was undertaken. There are no previous reports in the literature of electron exchange between heteropoly complexes and it seemed desirable to determine how readily an electron from the central atom could penetrate the extensive tungsten–oxygen "cage." Moreover, this system seems to conform to the assumptions of Marcus' theory[5–7] for predicting the rates of electron exchange. Because they are generally very fast, very few anionic electron-exchange systems have been investigated thoroughly.[8]

## Experimental

**Chemicals.**—Reagent grade chemicals were used without further purification for the preparation of the potassium salt of anion I.[3] Anion II was prepared electrolytically as follows. A 0.02 $M$ solution of anion I was placed in the anode compartment of an "H" cell, which was used to prevent hydrogen, formed at the anode, from reducing anion II. The electrolysis was

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(1) Supported by the U. S. Atomic Energy Commission under grant No. AT(11-1)-1001.

(2) To whom correspondence should be addressed.

(3) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).

(4) L. C. W. Baker and V. E. Simmons, *ibid.*, **81**, 4744 (1959).

(5) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

(6) R. A. Marcus, *ibid.*, **26**, 872 (1957).

(7) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(8) D. R. Stranks, Chapter 2 in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 163.

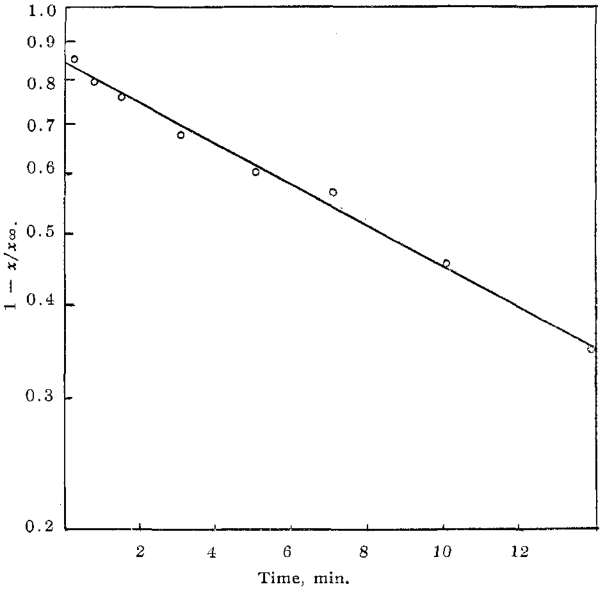

Fig. 1.—Typical rate data: temperature 0°; 0.4 $M$ LiCl; [I] = $1.14 \times 10^{-3}$ $M$; [II] = $1.22 \times 10^{-3}$ $M$; $k = 0.44$ $M^{-1}$ sec.$^{-1}$.

carried out at a platinum anode with an applied potential of 4.5 v. The entire cell was immersed in water at 80°.

Potassium in the stock solution was replaced with lithium by the use of Dowex 50W-X12 cation-exchange resin. The concentration of sodium plus potassium was determined by flame photometry to be less than 10 p.p m. In addition this procedure removes any cationic cobalt which may be present.

**Analysis**—The anion II concentrations were determined by potentiometric titration with ferrous ammonium sulfate, which quantitatively reduces anion II to anion I. The anion I concentrations were similarly determined by electrolytic oxidation and titration of the anion II which formed. The method has several advantages over analysis of the solid materials, in that it requires no knowledge of the somewhat uncertain number of cations or protons present in these acid salts or of the number of waters of crystallization, but gives the concentration of the anions (I or II) directly.

**Tracer.**—$^{60}$Co (5.2-year) was obtained from the Oak Ridge National Laboratory and 0.5 mc. was introduced during the preparation of the stock solution of anion I. Counting of the separated precipitates was done with a windowless gas-flow counter, using "Q gas" (helium–isobutane) and an applied potential of 1400 volts.

**Procedure and Separation.**—One ml. of a solution of anion I was prepared with the necessary HCl and/or lithium or potassium chloride and was stored at the ambient temperature of the reaction. Similarly the anion II stock and all glassware were stored at the proper temperature. The reaction was started by pipetting the 1 ml. of anion II solution into the anion I. A new solution mixture was prepared for each point, because of the rapid rates and our inability to take and separate enough aliquots from a single reaction mixture. Black-painted test tubes served as the vessels, although no evidence of photochemical acceleration was found when reactions were run in unpainted tubes.

Anion II was then precipitated by addition of the separation–quenching solution (1 ml.) to the reaction mixture. The quenching reagent contained 75% by volume of a solution saturated at 25° with $(C_4H_9)_4NI$, and 25% by volume sodium acetate–acetic acid solution (0.1 $M$ in acid and salt), plus 0.1% by weight "Celite" filter aid. In order to avoid the precipitation of both anions, at higher temperatures, it was necessary to decrease the amount of quenching reagent. For highly acid runs, additional sodium acetate was required. The quenching reagent was used at 0° to reduce separation-induced exchange. The quenched solutions were filtered on Whatman No. 540 filter paper in a funnel with a removable chimney, and the resulting precipitates were air dried and counted. Separation-induced exchange to the extent of about 20% was observed in most runs but remained approximately constant for runs at a given set of conditions. Early attempts at using $(CH_3)_4NI$ in the quench led to even greater induced exchange.

Originally specific activities of the precipitates were measured, but sample weights were sufficiently reproducible that only total counts for the precipitates were taken for most of the calculations.

## Results

The data were obtained by carrying out the separation described above at various times and determining the activity of the resulting precipitates. The rate of the exchange is given by the McKay equation,[9] as shown graphically in Fig. 1 for some typical rate data. It was found that, for the conditions in Table I

$$R = k[\mathrm{I}]^{\alpha}[\mathrm{II}]^{\beta}$$

$k = 0.63 \pm 0.016$, $\alpha = 1.0 \pm 0.01$, and $\beta = 1.01 \pm 0.01$. The half-time was approximately 8 min.

Table I

Dependence of the Rate Constant on Reactant Concentrations

Ionic strength adjusted to 0.6 with LiCl; temp. 0°; Li salts of anions I and II; pH 2

| [I], $M$ | [II], $M$ | $k$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|
| 0.0007 | 0.0018 | 0.63 |
| 0.0009 | 0.0015 | 0.64 |
| 0.0011 | 0.0012 | 0.63 |
| 0.0014 | 0.0010 | 0.65 |
| 0.0016 | 0.0007 | 0.61 |
| | | 0.63 ± 0.016 |

Because the heteropoly acid salts used in this investigation can ionize, it was necessary to determine what the effect of hydrogen ion concentration was on the rate.

The hydrogen ion concentration was varied from 0.025 to 0.80 $M$ with HCl while the ionic strength was maintained constant at 1.02 with LiCl, Table II. (The activity coefficients of LiCl and HCl are nearly identical in this concentration range.) Within experimental error (±6%) the rate constant was independent of hydrogen ion concentration at constant ionic strength.

Table II

Dependence of Rate Constant on HCl Concentration

$\mu = 1.02$ adjusted with LiCl; [I] = $1.08 \times 10^{-3}$ $M$; [II] = $1.22 \times 10^{-3}$ $M$; temp. 0°

| HCl, $M$ | $k$, $M^{-1}$ sec.$^{-1}$ |
|---|---|
| 0.025 | 1.05 |
| 0.200 | 0.98 |
| 0.400 | 1.03 |
| 0.600 | 0.93 |
| 0.800 | 1.09 |

The rate was found to have a marked dependence on ionic strength. The ionic strength was varied from 0.015 to 0.81 by the addition of LiCl. The pH was 2, due to the ionization of the acid salts. The results are summarized in Table III. Ionic strength was calcu-

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[9] H. A. C. McKay, *Nature*, **142**, 997 (1938).

lated using 3 × 3 as the charge product of anions I and II, since 3 × 3 = 9 is closer to the experimental value of $z_1z_2$ = 8 than 2 × 3. It seemed doubtful that the charges would differ by two units, so $z_1z_2$ = 2 × 4 was not considered.

TABLE III

DEPENDENCE OF THE RATE CONSTANT ON THE IONIC STRENGTH

Ionic strength adjusted with LiCl; temp. 0°; [I] = 1.14 × $10^{-3}$ $M$; [II] = 1.22 × $10^{-3}$ $M$

| $\mu$ | $\sqrt{\mu}$ | $\kappa r$ | $e^{-\kappa r}$ | $k$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|
| 0.015 | 0.122 | 0.396 | 0.670 | 0.03 |
| 0.05 | 0.224 | 0.727 | 0.481 | 0.07 |
| 0.21 | 0.459 | 1.489 | 0.225 | 0.31 |
| 0.41 | 0.641 | 2.080 | 0.125 | 0.44 |
| 0.61 | 0.783 | 2.541 | 0.079 | 0.64 |
| 0.81 | 0.901 | 2.924 | 0.053 | 0.96 |

Using a Debye–Hückel type treatment, but taking into account the charge separation distance, $r$, for large ions, Marcus[10] predicts, as described below, that a graph of ln $k$ vs. $e^{-\kappa r}$ should give a straight line with slope proportional to $z_1z_2$, the charge product of the ions in solution. Extrapolation to $\mu$ = 0 gives $k_0$ = 4.5 × $10^{-3}$ $M^{-1}$ sec.$^{-1}$.

The temperature dependence of the rate was studied at several ionic strengths and the parameters of activation were obtained. $E_a$, the activation energy, is a function of ionic strength, and an approximate extrapolation to $\mu$ = 0 was possible. The transition state equation, with the transmission coefficient taken as 1, was used (Fig. 2) to obtain the values of $\Delta S^*$ in Table IV.

TABLE IV

DEPENDENCE OF THE RATE CONSTANT ON TEMPERATURE AND IONIC STRENGTH

Ionic strength adjusted with LiCl; [I] = 1.14 × $10^{-3}$ $M$; [II] = 1.22 × $10^{-3}$ $M$

| $\mu$ | $k$, $M^{-1}$ sec.$^{-1}$ | Temp., °C. | $E_a$, kcal./mole | $\Delta S^*$, e.u. |
|---|---|---|---|---|
| 0.21 | 0.31 | 00.0 | | |
| 0.21 | 0.48 | 12.7 | 5.0 ± 0.5 | −44.0 ± 2 |
| 0.21 | 0.72 | 25.0 | | |
| 0.05 | 0.07 | 00.0 | | |
| 0.05 | 0.13 | 12.7 | 8.0 ± 1 | −35.4 ± 1 |
| 0.05 | 0.34 | 25.0 | | |
| 0.015 | 0.03 | 00.0 | | |
| 0.015 | 0.08 | 12.7 | 12.8 ± 2 | −19.7 ± 2 |
| 0.015 | 0.24 | 25.0 | | |
| 0.00 | ... | ... | 18 (extrapolated) | |

Substitution of the lithium cations by potassium ions leads to large increases in the rate of electron exchange as shown by the data in Table V. The half-time is only 0.73 min. for solutions 0.3 $M$ in KCl. This represents the approximate lower limit of half-times which we can measure with our method. Attempts to test the effect of cesium ion led to some precipitation of the heteropoly ions by cesium.

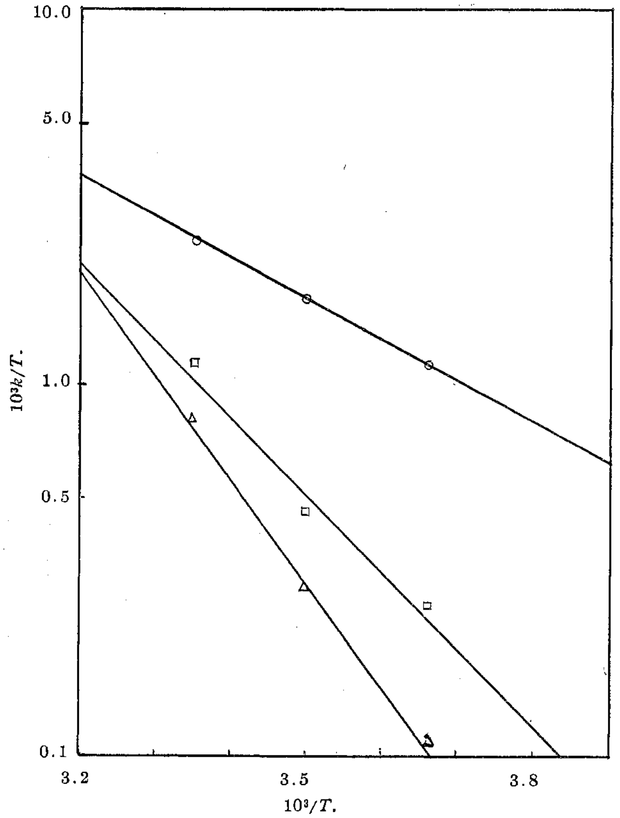

Fig. 2.—Log $k/T$ vs. $1/T$: upper curve, $\mu$ = 0.22 $M$; middle curve, $\mu$ = 0.06 $M$; lower curve, $\mu$ = 0.02 $M$; [I] = 1.14 × $10^{-3}$ $M$; [II] = 1.22 × $10^{-3}$ $M$.

TABLE V

DEPENDENCE OF THE RATE CONSTANT ON VARIOUS CATIONS

[I] = 1.14 × $10^{-3}$ $M$; [II] = 1.22 × $10^{-3}$ $M$; Temp. 0°; $K^+$ added as KCl

| Cation | Concn., $M$ | $k$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|
| Li | 0.015 | 0.03 |
| Li | 0.05 | 0.07 |
| Li | 0.21 | 0.31 |
| Li | 0.41 | 0.44 |
| Li | 0.61 | 0.64 |
| Li | 0.81 | 0.96 |
| K | 0.02 | 0.74 |
| K | 0.10 | 2.21 |
| K | 0.30 | 6.67 |

In order to determine the effect of dielectric constant on the rate, several runs were made in dioxane–water mixtures. Data on the dielectric constant of such mixtures are not available for 0°, but suitable values were obtained by extrapolation of the data which are available for temperatures from 15 to 45°.[11] Since the density of 1,4-dioxane is 1.03 ($d^{20}{}_4$) we may substitute volume per cent for weight per cent for our purposes. Decreasing the dielectric constant caused a substantial decrease in the rate, but it was not possible, due to the solubility of the precipitated anion II, to carry out the separation at very low values of the dielectric constant.

According to Marcus,[10] ln $k$ is plotted vs. $1/D_s$. From the slope, the charge product is estimated, $z_1z_2$

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[10] R. A. Marcus, private communication.

[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1958, p. 713.

TABLE VI

DEPENDENCE OF THE RATE CONSTANT ON THE DIELECTRIC CONSTANT

Temp. 0°; $\mu = 0.6\ M$ (adjusted with LiCl); [I] $= 1.14 \times 10^{-3}\ M$; [II] $= 1.22 \times 10^{-3}\ M$

| Vol. % dioxane | $D_s$ | $1/D_s$ | $k$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|---|
| 0.0 | 88.0 | 0.0114 | 0.63 |
| 4.0 | 84.3 | 0.0119 | 0.52 |
| 20.0 | 69.3 | 0.0144 | 0.36 |
| 32.0 | 57.0 | 0.0175 | 0.26 |

$\approx$ 30. However, these data (Table VI) are for $\mu = 0.6\ M$ and not for very dilute solutions.

## Discussion

Because of the structure and stability[12] of anions I and II, it seems unlikely that tungstate units are substitutionally labile. The ions appear to conform to the criteria necessary to the theory of Marcus,[10] which is derived specifically for the case of weak overlap and should obtain with such large anions (about 10 Å. diameter). According to Marcus

$$k = Z \exp[-\Delta F^*/RT]$$

where $Z = 10^{11}\ M^{-1}$ sec.$^{-1}$ and

$$\Delta F^* = \frac{z_1 z_2}{r D_s} e^{-\kappa r} + m^2 \lambda$$

where $m = -0.5$ for electron exchange reactions ($\Delta F^\circ \approx 0$) and

$$\lambda = \lambda_i + \lambda_0$$

$$\lambda_0 = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right)(\Delta e)^2$$

$$\lambda_i = \sum \frac{k_j k_j{}^p}{k_j + k_j{}^p} (\Delta q^0{}_j)^2$$

where $n$ is the refractive index of the solvent, $D_s$ is the dielectric constant of the solvent, $a_1$ and $a_2$ are the radii of the reactants, $r = a_1 + a_2$, $\Delta e$ is the electronic charge transferred, $\Delta q^0{}_j$ is the change in equilibrium bond length of bond j, and $k_j$ is the force constant of bond j.

For the $Co^{II}O_4$, $Co^{III}O_4$ tetrahedra, which form the core of the heterpolyions used in this study, only one of the normal coordinates is significantly different for the two ions—the one corresponding to bond length change.[13] The summation is over all four bonds and for both reactants. All the other $\Delta q^0{}_j$ should be nearly zero in a case where the reactants and products are so similar. In order to estimate the $\Delta q^0{}_j$, which corresponds to bond length change, one may use the crystal radii of Pauling[14] with a ligancy correction from six to four which give: $Co^{II}$–O = 1.97 Å. and $Co^{III}$–O = 1.87 Å. The latter value has been found to be 1.88 Å. in $K_5[Co^{III}O_4W_{12}O_{36}]$ by X-ray diffraction.[15] Using both of the calculated values for consistency, $\Delta q^0 \approx 0.1$ Å. "Badger's rule" was used to evaluate the force constants[16,17]: $k_{Co^{II}-O} = 1.66 \times 10^5$ dynes/cm. and $k_{Co^{III}-O} = 2.27 \times 10^5$ dynes/cm. Substituting these values into the $\lambda_i$ equation yields $\lambda_i = 7.68 \times 10^{-13}$ erg. Using $a_1 + a_2 = 10$ Å. and $z_1 z_2 = 8(4.8 \times 10^{-10})^2$ e.s.u., we obtain $\Delta F^* = 10.4$ kcal./mole and $k = 4.7 \times 10^2\ M^{-1}$ sec.$^{-1}$ from the Marcus theory, which compares with the experimental value for the low ionic strength limit, $k_0 = 4.5 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$ at 0°.

Rates determined experimentally are about $10^{-5}$ or $10^{-6}$ of those calculated from the Marcus theory. It appears that too many simplifying assumptions may have been required for the calculation, or that this system does not exactly meet the requirements of the theory. Here the central ions are surrounded by $WO_4$ octahedra rather than by O atoms, and transfer of electrons across the octahedra may not be equivalent to transfer in simpler oxy anions.

The dependence of the rate on the cation concentration for $Li^+$ and $K^+$ is linear in the narrow range studied, hence one might write

$$R = k[M^+][I][II]$$

However, since the acceleration is specific for $Li^+$ and $K^+$ ($Cs^+$ and $(C_4H_9)N^+$ cause precipitation), it appears that the effect is due mostly to increased ion pairing by the larger $K^+$ ion. Although the activated complex is of uncertain structure in "outer-sphere" reactions, the data would seem to indicate that closeness of approach is very important in determining whether or not electron exchange occurs.

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[12] V. E. Simmons, Ph.D. Dissertation, Boston University, 1963, p. 175.

[13] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Co., New York, N. Y., 1945, p. 100.

[14] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 518, 535.

[15] N. F. Yannoni, Ph.D. Dissertation, Boston University, 1961.

[16] R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

[17] R. M. Badger, *ibid.*, **3**, 710 (1935).