

$$\Delta \bar{F}_1 = \bar{F}_1 - \bar{F}_1^0 = gRT \ln X_1 = -\frac{\varphi RT 2m}{1000/M_1} \quad (8)$$

$$(\Delta \bar{F}_2)_{\text{non-ideal}} = 2RT \ln f \quad (9)$$

$$\log \gamma = \log f - \log (1 + 2mM_1/1000) \quad (10)$$

where  $g$  is the rational osmotic coefficient,  $\varphi$  is the practical osmotic coefficient,  $f$  is the rational activity coefficient,  $\gamma$  is the practical activity coefficient,  $m$  is the molality, and  $M_1$  is the formula weight of the solvent. These quantities may be calculated readily from the values of Tables III and IV.

A comparison of these results for osmotic and activity coefficients with those obtained from freezing point data by Scatchard and Prentiss,<sup>8</sup> isopiestic vapor pressure data at 25° by R. A. Robinson<sup>9</sup> and unpublished isopiestic vapor

(8) Scatchard and Prentiss, *THIS JOURNAL*, **55**, 4355 (1933).

(9) R. A. Robinson, *ibid.*, **57**, 1161 (1935).

pressure data at 30 and 40° by R. A. Robinson shows the same type of agreement as in the case of solutions of sodium chloride.<sup>5,6</sup> The agreement is satisfactory for concentrations to 1.5 molal; at higher concentrations and at temperatures near 60°, the activity coefficients determined from the boiling point elevations are high relative to those obtained by the other methods.

### Summary

1. Boiling point elevations of solutions of potassium bromide in water have been determined to 5.0 molal over the range 60–100°.

2. Partial molal free energies have been calculated from these boiling point values. The method of calculating activity and osmotic coefficients has been indicated.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## The Exchange of Oxalates of Some Complex Trioxalate Ions of Trivalent Metals

BY F. A. LONG

Many trivalent metal ions form complex salts with alkali oxalates of the general formula  $\text{Alk}_3\text{M}(\text{C}_2\text{O}_4)_3$ . These complex oxalate salts are similar in many properties. They are very soluble in water, ionize to give alkali and complex oxalate ions, and show similar crystal forms.<sup>1</sup> In 1912 Werner<sup>2</sup> was able to resolve potassium chromium trioxalate into its optical isomers. Since then attempts have been made to resolve other analogous oxalate salts and in most cases the attempts have been successful. Complex oxalate salts of the following trivalent metal ions have been reported as capable of resolution into optical isomers: chromic,<sup>2</sup> cobaltic,<sup>3</sup> ferric,<sup>4</sup> aluminum,<sup>5</sup> rhodium,<sup>6</sup> iridium,<sup>7</sup> and gallium.<sup>8</sup> In addition resolutions have been reported for complex salts involving dibasic acid ions other than oxalate.

(1) Jaeger, "Optical Activity and High Temperature Measurements," Chapter VIII, McGraw-Hill Co., New York, N. Y., 1930.

(2) Werner, *Ber.*, **45**, 3061 (1912).

(3) Jaeger and Thomas, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **21**, 693 (1919). Johnson and Mead, *Trans. Faraday Soc.*, **29**, 626 (1933).

(4) Thomas, *J. Chem. Soc.*, **119**, 1140 (1921). See, however, Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

(5) Wahl, *Ber.*, **60**, 399 (1927). Burrows and Lauder, *THIS JOURNAL*, **53**, 3600 (1931).

(6) Werner, *Ber.*, **47**, 1954 (1914).

(7) Delépine and Bruhat, *Bull. soc. chim.*, [4] **17**, 223 (1915); Jaeger, *Rec. Trav. Chim.*, **38**, 270 (1919).

(8) Neogi and Dutt, *J. Indian Chem. Soc.*, **15**, 83 (1938).

For many years the assumption was tacitly made that any similar salt could be resolved into its optical isomers. Recently this assumption was challenged by C. H. Johnson<sup>9</sup> from the standpoint of the types of bonds involved in coordination compounds.

Pauling<sup>10</sup> has discussed the bond type for various coordination compounds and has shown that for many such compounds the bonds approach rather closely to one or the other of the two types, covalent bonds or ionic bonds. If there are available for bonding two  $d$ , three  $p$  and one  $s$  orbital, then strong  $s-p-d$  hybrid bonds directed toward the apices of a regular octahedron can be formed provided that the increased bonding energy can more than offset any loss of energy due to change of multiplicity. Magnetic susceptibility measurements will often give an indication of the bond type but this criterion is, of course, useful only when a change of multiplicity occurs as the bond type changes from primarily ionic to primarily covalent. For instance chromic ion complexes will give the same susceptibility whether the bonding is covalent or ionic, as may

(9) Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

(10) "The Nature of the Chemical Bond," Chapters II and III, Cornell University Press, Ithaca, N. Y., 1939.

be gathered from Fig. 1 which gives a schematic representation of the electron structures of the trivalent ions of aluminum, chromium, iron and cobalt.

Johnson determined the magnetic susceptibilities of several of the complex oxalate salts. The results for potassium cobaltioxalate indicate that the bonds are covalent. The results for the chromioxalate salt do not allow a distinction to be made. But potassium ferrioxalate has a magnetic susceptibility very similar to that of the ferrifluoride salt, indicating ionic bonds. The magnetic susceptibility offers no criterion for potassium aluminum oxalate since aluminum ion has a rare gas structure, but in this case the  $d$  orbitals necessary for  $s$ - $p$ - $d$  bonding are so far away that such bonding is very unlikely.

	3s	3p	3d	4s	4p
Al <sup>+++</sup>	□	□□□	□□□□□	□	□□□
Cr <sup>+++</sup>	⊙	⊙⊙⊙	⊙.⊙.⊙	□	□□□
Fr <sup>+++</sup>	⊙	⊙⊙⊙	⊙.⊙.⊙.⊙	□	□□□
Co <sup>+++</sup>	⊙	⊙⊙⊙	⊙.⊙.⊙.⊙	□	□□□

Fig. 1.—Electrons present in the various orbits for some trivalent ions. The 1s, 2s and 2p orbits are filled in all cases.

By far the greatest number of optically active coordination compounds have been found where covalent bonds are probable. On the basis of this and the magnetic susceptibility results, Johnson made two very interesting suggestions. First, the chromioxalate complex involves covalent bonds. Second, the necessary stability to allow resolution of these complex salts into optical isomers will only result when the bonds are covalent. Pursuing this argument, Johnson attempted to resolve the complex oxalate salts of ferric and aluminum ions and did not succeed in spite of the fact that they had previously been reported to be resolvable.

One of the complicating properties of the optically active isomers of complex oxalate salts is a frequent racemization of the complex ion in solution. This was once thought to indicate an ionization of the complex ion. Recent work,<sup>11</sup> however, has shown that for potassium chromioxalate this racemization is not the result of an ionization but rather is due to some sort of an intramolecular rearrangement. The proof of this was that

the chromioxalate ion in solution does not interchange oxalates with other oxalate ions even under conditions where the racemization would be rapid.

This fact, that the chromioxalate ion is stable to interchange of oxalates, suggests a method of obtaining additional information on the postulates of Johnson. This is simply to examine other similar oxalate complexes with respect to interchange of oxalates and see if there are any sharp differences in stability. The interchange can be studied by using "marked" oxalate prepared from radioactive carbon. The present paper reports results for the interchange of uncombined oxalate ions with the oxalate present in the trioxalato ions of ferric, aluminum and cobaltic ions.

### Experimental

**Preparation and Purification of Compounds.**—Potassium cobaltioxalate was prepared according to the directions of Thomas.<sup>12</sup> The salt was reprecipitated from aqueous solution with excess ethyl alcohol and then recrystallized from water. Analysis for oxalate and water content checked with the formula,  $K_3Co(C_2O_4)_3 \cdot 3H_2O$ . Aqueous solutions gave no precipitate with either silver or calcium ions. Since the salt is unstable with respect to photochemical decomposition it was stored in the dark and its solutions were kept in darkened vessels.

Potassium ferrioxalate was prepared by heating together in concentrated solution the correct proportions of ferric chloride and potassium oxalate. The complex salt precipitated from this solution upon the addition of excess ethyl alcohol. It was purified by reprecipitation with ethyl alcohol. It was analyzed for oxalate and water content and gave satisfactory results. All samples of the salt, even after several recrystallizations give in solution an immediate precipitate with silver ion. With fairly large amounts of calcium ion no precipitate forms at first but a slight cloudiness forms after several minutes. This salt is also photochemically unstable and was treated with the same precautions as the potassium cobaltioxalate.

Potassium aluminum trioxalate was prepared by adding an excess of freshly precipitated aluminum hydroxide to an equimolar solution of potassium oxalate and oxalic acid. After a period of digestion and concentration the excess aluminum hydroxide was filtered off and the complex salt precipitated from the cooled solution. The salt was recrystallized twice from water and gave a product that showed the calculated oxalate content. Aqueous solutions gave a slight precipitate with both calcium and silver ions after several minutes.

**Determination of Interchange.**—The general method of determining the interchange of oxalate between the complex oxalate ions and uncombined oxalate ions was to mix a solution of the complex salt with a solution of potassium oxalate that had been synthesized from the short-lived radio-carbon, C<sup>14</sup>. After an interval of time the uncombined oxalate was removed by precipitation as silver or

(11) F. A. Long, *THIS JOURNAL*, **61**, 570 (1939).

(12) Thomas, "Complex Salts," p. 117. Blackie and Son, London, 1924.

calcium oxalate. A comparison of the radioactivity of this with the radioactivity of silver or calcium oxalate prepared from the original potassium oxalate indicates the amount of interchange. In addition, the amount of radioactivity in the complex salt was determined whenever possible.

The method of preparing potassium oxalate which contains radio-carbon and the method of measuring the radioactivity have already been reported for the earlier work with potassium chromioxalate.<sup>11</sup> The experimental results for the individual compounds, together with any differences in procedure are given below.

**Potassium Cobaltioxalate.**—Two determinations of the interchange were made, one at 35° and one at 50° but both using a solution of 0.06 *M* cobaltioxalate ion and approximately 0.012 *M* radioactive potassium oxalate. For each run 100 ml. of about 0.025 *M* radioactive potassium oxalate was divided into two portions of 25 ml. and 75 ml. The smaller was precipitated as silver oxalate and filtered. The precipitate was labeled Sample I, the control sample. The remaining 75 ml. was mixed with 75 ml. of 0.12 *M* potassium cobaltioxalate and kept at a constant temperature of either 35 or 50°. Three equal portions of this mixture were removed, one at the time of mixing, the second twelve minutes after mixing and the third twenty-five minutes after. The uncombined oxalate in each of these was precipitated as silver oxalate and filtered off. These precipitates were labeled Sample II, Sample III, and Sample IV, respectively. The filtrate from Sample IV, containing the potassium cobaltioxalate was treated with excess hexamine cobaltinitrate and the resulting precipitate of hexamine cobaltcobaltioxalate was filtered and labeled Sample V. The radioactivities of these samples, the four equal samples of silver oxalate and the precipitated cobaltioxalate salt, were then determined. The results are given in Table I and show that within the experimental error there is no exchange of oxalate between free oxalate ions and those in cobaltioxalate ions.

TABLE I

A COMPARISON OF THE RADIOACTIVITY FOR THE COBALTI-OXALATE INTERCHANGE

The times for each sample are for the time at which the sample was withdrawn from the mixture of cobaltioxalate and oxalate ions. The figures give a comparison at a single time of the radioactivity for the samples for each run. The units are divisions of swing of the galvanometer. Sample V is the  $\text{Co}(\text{NH}_3)_6\text{Co}(\text{C}_2\text{O}_4)_3$  formed from the filtrate of Sample IV.

Sample	I	II	III	IV	V
Time, min.	Control	0	12	25	25
Run at 35°	9.10	8.60	8.35	8.25	0.01
Run at 50°	3.5	3.4	3.4	3.4	.0

**Potassium Ferrioxalate.**—Experiments similar to the cobaltioxalate ones showed that this salt, in sharp contrast to the cobalt salt, exchanged oxalates with great rapidity. Qualitatively these experiments showed the ferrioxalate-oxalate interchange to be both rapid and complete. However the original procedure did not give quantitative results since investigation showed that excess calcium ion tended to precipitate some of the ferrioxalate along with the added oxalate. Hence it was necessary to change the procedure both to eliminate this and to attempt to obtain data on the speed of the interchange.

The procedure that was finally adopted and which proved fairly successful was to remove only a given fraction of the uncombined oxalate by precipitating with somewhat less calcium chloride than the amount necessary for complete precipitation. If the pH of the final mixture is kept within 4.5 to 6 it is possible to take a mixture of oxalate and ferrioxalate, add about two-thirds the amount of calcium chloride that would be equivalent to the oxalate alone and obtain a precipitate of calcium oxalate that is within 2 or 3% of the amount expected. This means that a determination of the completeness of interchange can be carried out by precipitating in all cases only a certain equal fraction of the added, uncombined oxalate. The actual procedure for a determination of this type, for which the results are given in Table II, was as follows. A solution of 100 ml. of radioactive potassium oxalate was prepared as usual except that the pH of the solution was kept between six and seven. An aliquot of 25 ml. was titrated with standard potassium permanganate solution and showed the concentration of the potassium oxalate to be 0.0296 *M*. Therefore a 25-ml. portion of this solution would take 7.80 ml. of 0.095 *M* calcium chloride to just precipitate the oxalate. Consequently another 25-ml. portion of the potassium oxalate was added to 75 ml. of hot solution containing just 5 ml. of 0.095 *M* calcium chloride. The precipitated calcium oxalate was filtered off and constituted Sample I, the control sample. The remaining 50 ml. of potassium oxalate was mixed rapidly with 50 ml. of 0.06 *M* potassium ferrioxalate and 50 ml. of this mixture was added rapidly to 50 ml. of hot solution again containing just 5 ml. of 0.095 *M* calcium chloride. The time between mixing and the start of precipitation was less than twenty seconds. The filtered calcium oxalate constituted Sample II. Sample III was obtained in a fashion identical with II, but was precipitated fifteen minutes after mixing. Sample IV is precipitated potassium ferrioxalate resulting from the addition of the filtrate from III to excess ethyl alcohol. Three samples of calcium oxalate were thus obtained from equal volumes of solution which contained identical amounts of calcium ion and identical excess amounts of uncombined oxalate ion. The only difference is the presence of ferrioxalate in two of the solutions.

TABLE II

THE FERRIOXALATE INTERCHANGE

Sample IV is the  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$  recovered from the filtrate of Sample III.

Sample	I	II	III	IV
Time	Control	0	15	15
Radioactivity	10.6	1.43	1.50	8.8

The data of Table II again show clearly that interchange has taken place. The marked difference in the radioactivity of the control sample and of the other two samples of calcium oxalate shows this as does also the radioactivity of the precipitated potassium ferrioxalate. In a solution of 0.03 *M* ferrioxalate and 0.0148 *M* added oxalate, complete interchange would give a ratio of radioactivities in the uncombined oxalate before and after mixing of 0.1048 to 0.0148 or 7.08. The ratio of the radioactivities of the control sample, I, and the average of samples II and III is 7.24. This agreement is well within the rather large experimental error so that this experiment indicates that there is a rapid

and complete interchange of oxalates between free oxalate ions and those in ferrioxalate ion.

It is not easy to decide whether these results are really quantitative or not. The fact that ferrioxalate ion solutions are not stable to calcium ion makes the quantitative aspects somewhat dubious. However, the later experiments, as exemplified by Table II, seem to be straightforward and give, to say the least, a semi-quantitative proof of the completeness of interchange.

**Potassium Aluminum Trioxalate.**—The experimental procedures and results for this salt were almost identical with those for the ferrioxalate salt. Several preliminary determinations of the interchange were made and they all suggested a rapid and complete interchange but here also there was some trouble in getting a quantitative proof. However, a procedure similar to that finally used for the ferric compound gave satisfactory results. In fact the only difference in the two cases was that it was impossible to recover the potassium aluminum trioxalate from the reaction mixture.

Table III gives the results for a run which was almost identical with the one that is shown in Table II for the ferrioxalate. The temperature, the time for mixing and for withdrawal of samples and the general procedure were identical. The concentration of the original 100 ml. of radioactive potassium oxalate was very similar, 0.0292 *M*, and that for the aluminum trioxalate ion was again 0.03 *M* after mixing. From the results, as shown in Table III, the ratio of the average of the radioactivities of Samples II and III to that of the control sample is 7.0. The calculated ratio for the given concentrations, assuming complete interchange is 7.1. This is a satisfactory check and indicates that for the aluminum salt also there is rapid and complete interchange between the uncombined oxalate ions and the oxalates in the complex ions.

TABLE III  
THE ALUMINUM TRIOXALATE INTERCHANGE

Sample	I	II	III
Time	Control	0	15
Radioactivity	30.4	4.49	4.32

### Discussion

These interchange experiments serve to divide the four rather similar complex oxalate salts into two different classes, the chromic and cobaltic salts which show no interchange and the aluminum and ferric salts which show very rapid and complete interchange. A consideration of the probable bond types makes this distinction seem reasonable. The magnetic data make covalent bonds rather certain for the cobaltioxalate complex and the fact that the necessary bonding orbitals are available for the chromium salt suggests that the complex, here also, involves covalent bonds. On the other hand, the magnetic susceptibility results for the ferric complex and the available orbitals in the case of aluminum make covalent bonds very unlikely. Thus there

is a rather suggestive correlation between interchange and bond type.

The results of these interchange experiments would, at first glance, seem to have an important bearing on the question of the optical activity of these salts since interchange would certainly supply a mechanism for the racemization of an optically active salt in solution. And there is some agreement between the present work, and the reported results on the optical activity. The fact that salts of the chromic and cobaltic complexes can be resolved is well established; these two salts show no interchange with uncombined oxalate ions. But for the ferric and aluminum complexes, which exhibit a rapid interchange reaction, the data on optical activity are rather inconclusive.

Thomas<sup>4</sup> reported the resolution of potassium ferrioxalate and stated that the optically active salt was somewhat stable in aqueous solution. At room temperature the half-time for its autoracemization was about fifteen minutes. Johnson,<sup>9</sup> however, was unable to repeat these results and concluded that the salt was incapable of resolution. Johnson was also unable to resolve salts of the aluminum trioxalate complex although resolutions had previously been reported by Wahl<sup>6</sup> and by Burrows and Lauder.<sup>5</sup> These last two investigations indicated, moreover, that the optically active aluminum complex is comparatively stable in aqueous solution. The half-time of racemization at room temperature was reported as varying between thirty minutes and twenty hours.

Proof of a very rapid interchange would undoubtedly lend support to the conclusion that salts of the aluminum and ferric oxalate complexes are not capable of resolution, and the results of the present work do indicate rapid interchange. Unfortunately, however, the present results are not sufficiently good to allow a definite conclusion to be made. The interchange reaction is rapid under the given experimental conditions. At 25° and with concentrations of 0.03 *M* complex ion and 0.015 *M* uncombined oxalate ion the interchange, for both the aluminum and ferric complexes, is at least 90% complete in twenty seconds. But the conditions under which resolutions have been attempted and under which the stabilities of the optically active salts have been determined are considerably different. In this case the pure salt is dissolved in water and the only oxalate ion present as such is that which

results from the dissociation of the complex ion. The extent of the dissociation of these complex ions is not accurately known although Latimer<sup>13</sup> estimates a dissociation constant of around  $10^{-10}$  for the ferric oxalate complex. Considering this and also the fact that silver and calcium ions will form slight oxalate precipitates with both of the complex ions, it is probable that the oxalate ion concentration in a solution of 0.01 *M* complex ion is of the order of magnitude of  $10^{-4}$  *M*. Consequently an interchange reaction that is rapid under the conditions of the present investigation and a stability of the optically active complex of the extent reported by Thomas and Wahl are not entirely incompatible.

The present work, of course, sets only a lower limit to the speed of interchange. The speed could be very much faster and still be in accord with the interchange results. In this case the possibility of comparatively stable optical isomers could probably be ruled out. Attempts have been made to study the interchange reaction under conditions more nearly comparable to the conditions under which the optical activity has been studied. This involves concentrating the radio-carbon in much smaller amounts of potassium oxalate and then studying the interchange

(13) "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 212.

with only a minute amount of added oxalate. So far these attempts have not been successful. Thus the present work, although it makes the possibility of a stable optically active complex quite unlikely, does not suffice to eliminate the possibility of an optically active ion with a short life in aqueous solution.

### Summary

The interchange of oxalates between uncombined oxalate ions and complex oxalate ions of aluminum, ferric and cobaltic have been studied using radio-carbon. Under the given experimental conditions the ferric and aluminum trioxalate complexes show a rapid interchange. The cobaltic complex, like the previously studied chromic complex, shows no interchange. These results are in accord with the assumption that the bonds in the chromic and cobaltic complexes are probably primarily covalent whereas those in the ferric and aluminum complexes are ionic.

The possibility of the resolution of the ferric and aluminum trioxalate salts into their optically active isomers has been discussed in the light of the present work and it is concluded that a stable optically active ion is unlikely. However, the present work does not exclude the possibility of a short-lived optically active ion.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE BAILEY CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

## A Precision Method for the Determination of Molecular Weights

BY H. P. CADY AND M. J. RARICK

We have developed a method and apparatus<sup>1</sup> for the very rapid and yet precise determination of the molecular weights of gases and vapors. By means of this instrument the molecular weights may be read directly without any calculations, and on pure substances results reproducible to 0.01 of a unit of molecular weight may be obtained.

The only measurement involved is the determination of the flotation effect of the gas or vapor on a sealed body of known volume, at a temperature automatically adjusted to the momentarily existing atmospheric pressure in such a manner that a constant gaseous density is maintained.

(1) U. S. Letters Patent No. 2,023,164.

### Apparatus

We have found a special chainomatic balance of the Westphal type very satisfactory for measuring the flotation. The balance is easily sensitive to 0.02 mg. and is graduated in units equivalent to 2 mg. A working temperature of around 200° was chosen simply because this temperature is above the boiling point of most liquids. The volume of the float is made such that an ideal gas having a molecular weight of 1.00 would exert, at a pressure of around 740 mm. and a temperature of about 200°, a flotation of 2.00 mg. on the sealed bulb. Calculations indicate that the bulb should have a volume of about 80 cc. It is evident that 80 cc. of an ideal gas having a molecular weight