inserted between the side of the dish and the paraffin, loosens the block and it readily drops out if the dish be inverted. The block may be trimmed immediately, or, slipped back into the original vial and left indefinitely.

By regulating the temperature of the paraffin at the time of casting, the worker may have his material either distributed evenly through the block or the eggs may be allowed to settle enmasse to the bottom of the dish.

Comparatively few eggs are lost when this method is followed. It is especially advantageous when lots of fifty or a hundred stages have to be carried through, since there is a minimum probability of different lots mixed, and the material is on file from the moment of fixation.

R. J. BEAN
DALHOUSIE UNIVERSITY,
HALIFAX, NOVA SCOTIA

SPECIAL ARTICLES

THE CHLORIDES OF RUTHENIUM

A YEAR and a half ago[1] Mr. F. N. Mercer and I published a paper in which we described a method of separating ruthenium quantitatively by solution in sodium hypochlorite and distillation in a current of chlorine. At that time we had not found any simple way of analyzing the solution of pure ruthenium which distils over, reduction methods failing owing to the presence of free chlorine in the solution.

Since that time I have found that if the distillate is absorbed in concentrated hydrochloric acid, the solution can be titrated with stannous chloride, thus affording a simple method of determining small quantities of ruthenium, and also, by using aliquot portions, of evaluating solutions of ruthenium in chloro-ruthenate form.

The reaction depends upon the fact that ruthenium tetroxide, RuO_4, is reduced in hydrochloric acid solutions to quadrivalent form, and that dilute stannous chloride reduces quadrivalent ruthenium to trivalent ruthenium, and no farther, even under quite variable conditions. The change in color of the ruthenium solution from deep red to rose is quite recognizable, but for accuracy a slight excess of stannous chloride is added, and the solution titrated back with iodine solution, starch paste being used as an indicator.

There has been much discussion regarding the different valence states of ruthenium and especially as to what is formed when the volatile tetroxide is reduced by hydrochloric acid. When the tetroxide is boiled with hydrochloric acid and potassium chloride added, there crystallizes out a salt which has, since the days of Claus, its discoverer, passed as K_2RuCl_5, derived from the pentachloro-ruthenous acid, H_2RuCl_5, this in turn being a derivative of ruthenium trichloride, $RuCl_3$. From this it has been naturally assumed that the valence of ruthenium in this compound is three. On the other hand, Krauss, as well as Remy, have conclusively proved that the ruthenium in RuO_4, on reduction by hydrochloric acid, is reduced only four valences. It has therefore been assumed that $RuCl_4$ (H_2RuCl_6) is first formed, and that the $RuCl_3$ (H_2RuCl_5) is the result of further reduction.

The result of titration with stannous chloride, however, shows that the ruthenium in both H_2RuCl_6 and H_2RuCl_5 (as supposed) is quadrivalent, each being reduced a single valence to the real H_2RuCl_5. With KCl (or other alkali chlorides) $K_2RuCl_5(H_2O)$, first recognized by me in 1901[2] and then called an "aquo"-salt, is formed. This must be recognized as the true pentachloro-ruthenite, crystallizing with one molecule of water, as would be expected from the Werner theory.

This was suggested by Charonnat in 1925,[3] on the basis of the reduction of the (supposed) K_2RuCl_5 by potassium iodide, and the formation of the aquo-salt by the action of hydrochloric acid on the oxalate, $K_3Ru(Ox)_3$, in which the ruthenium is undoubtedly trivalent. No analyses were published, however, to substantiate this observation, which was unquestionably correct, and it seems to have been overlooked.

Since the K_2RuCl_6 can be formed by the recrystallization of the (supposed) K_2RuCl_5 from very concentrated hydrochloric acid, and the K_2RuCl_5 is formed when the K_2RuCl_6 is recrystallized from dilute, or even moderately strong hydrochloric acid, and since the valence of the ruthenium is the same in both salts, it is probable, as Charonnat assumes, that the pentachloride salt is actually a hydroxy-salt, K_2RuCl_5OH, formed from the hexa-salt, K_2RuCl_6, by hydrolysis.

It is interesting to note that within wide limits the hexachloro-ruthenate is hydrolyzed to the extent of one chlorine atom only and that this product in water, in absence of hydrochloric acid, is further hydrolyzed to $RuCl(OH)_3$, while the true pentachloro-ruthenite, ("aquo" salt), is hydrolyzed only to $RuCl_2(OH)$.[4]

Fuller details of this research will appear later in the *Journal* of the American Chemical Society.

JAS. LEWIS HOWE
WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VIRGINIA

---

[1] J. Amer. Chem. Soc., 47 (1925), 2926.

[2] *Ibid.*, 23 (1901), 781.

[3] Compt. rend., 181 (1925), 866.

[4] Lind and Bliss, *J. Amer. Chem. Soc.*, 31 (1909), 868.