tion range 0.2629, slightly below saturation, to 0.0108 of barium by weight. Three cells have also been measured at 15° and 35°.

3. The observed potentials are markedly higher than the values calculated by the concentration law. The data are extrapolated to infinite dilution and the activities of barium calculated. The free energies of transfer are computed.
4. The heats of transfer of barium are calculated. The temperature coefficient of electromotive force is apparently a function of the temperature and d^2E/dT^2 positive.
5. The data are applied to test the Cady equation.

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THE COLOR OF THE TERVALENT TITANIUM ION

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In inorganic chemistry as well as in organic chemistry there are methods which enable us in certain cases to deduce the color of a compound from its formula. Piccard and Thomas were able to predict that certain salts which are usually considered as colorless should be yellow when observed in sufficiently thick layers. This proved to be the case with cadmium iodide and with mercury dibromide.[1]

In the present paper we shall see the reverse case, that of an ion which is perfectly colorless although generally considered as being violet.

In the textbooks of inorganic chemistry we are told that—with the exception of certain complex salts which are yellow or green—tervalent titanium gives violet solutions. Incidentally, I have made the observation that the violet solution of titanium trichloride becomes much more strongly colored when one adds ammonium thiocyanate to it. Titanium thiocyanate is an intensely violet molecule or complex and the suspicion arose that perhaps titanium trichloride solutions may also owe their color not to the titanium ion but to the titanium trichloride molecule. We can easily confirm this hypothesis if we take two flat-bottom test-tubes with 2 cc. of a 0.025 N titanium trichloride solution in each. We place these tubes side by side while we look vertically down through them. Then if we add water to one of the test-tubes we immediately notice that the color in the dilute solution diminishes, and after an addition of 20 cc. of water the violet color has disappeared.[2] The law of Beer is not followed,[3] and it is proved

[1] Piccard and Thomas, *Helvetica Chim. Acta*, **6**, 1040 (1923).

[2] This phenomenon is not due to hydrolysis, because it can also be observed when we dilute with weak hydrochloric acid solution, so that the hydrogen-ion concentration remains constant or even increases. Also, hydrolysis would increase the color,

beyond any doubt that the tervalent titanium ion is colorless or nearly colorless (we have not yet observed very deep layers) and that the well-known violet color of titanium trichloride solutions is a molecular property of titanium trichloride or of a complex like $[TiCl_5]$. The addition of concd. hydrochloric acid represses the dissociation and the violet color reappears.

This experiment shows that the Ti^{III} ion, like the chloride ion, has a *latent color* according to the definition given by Piccard and Thomas.[4] Since the fluoride ion has no latent color at all, the addition of hydrofluoric acid to a solution of titanium trichloride should take its violet color away and indeed it does.

In our first publication we did not attempt to give any theoretical explanation for the described observations. We said: "Notre petite étude est purement empirique." Professor Fajans was kind enough to draw our attention to two of his publications[5,6] in which he gives a theoretical explanation of the fact that the color of a salt may change if one replaces in it a colorless ion by another colorless ion. To use his expressions we can formulate our observation with the following words.

The tervalent titanium ion is colorless, but titanium trichloride is colored, because the titanium atom deforms the electronic shells of the chloride ions.[7]

not decrease it, because OH has a much stronger latent color than Cl, and $Ti(OH)_3$ is nearly black. That the phenomenon is not due to oxidation or liberation of free hydrogen was shown by titration with permanganate. In both test-tubes exactly the same amount of $KMnO_4$ is needed to produce a pink coloration.

[3] When one makes the same experiment with a copper sulfate solution, one does not see any change of color, because it is the (hydrated) Cu ion which is blue. But the yellow lead iodide solution and the brown ferric thiocyanate solution lose their color on dilution.

[4] There are three kinds of ions: (1) the colored ion, the combinations of which are always colored regardless of what ions are combined with it, (2) the ion with latent color, which in combination with other ions of latent color may produce colored molecules, but in the free form is colorless and its combinations with ions of the third kind are colorless, (3) the colorless ion, which forms colorless compounds with other colorless ions and with ions which have only latent color.

[5] *Naturwissenschaften*, **11**, 167 (1923). This very important paper had appeared in the same year but before our paper. Fajans says in it that for the detection of proper color (Eigenfarbe) one must observe the fluoride, the sulfate or the perchlorate and that anhydrous Cu^{II}, Fe^{II} and Fe^{III} are colorless. As a rule the anhydrous fluorides, sulfates and perchlorates of any metal have the same color as the anhydrous ion of that metal.

[6] *Z. Elektrochem.*, **29**, 495 (1923). See also *Z. Physik*, **23**, 1 (1924). See also Meisenheimer, *Z. physik. Chem.*, **97**, 304 (1921).

[7] FeF_3 is colorless, because Fe^{III} has only latent color and F has no color at all. $FeCl_3$ is yellow, because both ions have latent color. The Fe ion has already deformed the electronic shells of the chloride ions. $FeBr_3$ is dark brown on account of the stronger latent color of the bromide ion. Its electronic shell is badly pulled out of shape by the iron. If we try to make FeI_3, the iron not only deforms the electronic shells of the iodide ion, but it removes one electron completely. The iodine becomes neutral (elementary iodine), and the iron bivalent. (See Fajans, especially his work on refraction and deformability of the electronic shells.)

Summary

The (hydrated) tervalent titanium ion is colorless, but it has a strong latent color, on account of which titanium trichloride is colored.

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THE ENTROPY OF AQUEOUS IONS

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A knowledge of the values of the entropies of aqueous ions would place at our command a powerful tool for the direct solution of a large number of thermodynamical problems, many of which otherwise are open only to the most roundabout methods of attack. The treatment of these fundamental entropies has long been deferred by workers in the field of thermodynamics, in part because of the large discrepancies existing in the experimental reaction heats that are involved in their calculation, and in part because of the general lack of information in regard to the entropies of compounds. It would seem, however, that a profitable start may now be made, using as a guide the approximate proportionality pointed out by Latimer[1] between the entropy of solution and the heat of solution of gaseous ions. It is the purpose of this paper to investigate this relation and to give from a survey of existing data a table of values for the entropies of the more important ions. A few typical examples will be given to illustrate the tremendous value of such a table of entropies in the simplification of the thermodynamics of solutions.

As a standard state for comparison we will adopt the hypothetical one molal solution, and define it as a one molal solution of the ions obeying the laws of the perfect dilute solution and the ions possessing the same partial molal heat content that they have at infinite dilution.

In our initial calculations we have no means of obtaining absolute values for the entropies of the individual ions, but must calculate the values as the sum of the entropies of equivalent weights of two ions of unlike charge, or the difference in the entropies of equivalent weights of two ions of like charge.

The sum of the entropies of two ions is most accurately determined from a knowledge of the entropy of a compound and the entropy change for the reaction; compound equals ions in hypothetical one molal aqueous solution. For example, the sum of the entropies of H^+ and Cl^- is equal to the entropy of hydrogen chloride plus the entropy of solution of hydrogen chloride. This latter quantity is obtained from the relation $\Delta S = (\Delta H - \Delta F)T$, where ΔH is the heat of solution of hydrogen chloride in an infinitely dilute

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[1] Latimer, This Journal, **48**, 1234 (1926).