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The effects of equal concentrations of the alkali and alkaline earth chlorides and of hydrogen chloride on the absorption spectra of aqueous cobalt chloride solutions have been studied. Solutions prepared both on the molar and on the molal bases were used. In all cases, the absorption bands widen with an increase in concentration of the added salt. The increase in width of the absorption bands varies directly as the ionic charge and inversely as the ionic volume of the added cation. The inadequacy of existing explanations of the well-known color changes in cobalt chloride solutions is discussed and a new explanation is offered.

THE influence of added salts on the color of cobalt chloride solutions has been studied by several investigators but no completely satisfactory explanation of the observed color changes has been given.

Vogel[1] reported anomalous changes in the absorption bands of cobalt chloride solutions with changes in concentration. Donnan and Bassett[2] suggested the existence of blue $CoCl_4^{--}$ ions and Macwalter and Barratt[3] carried out experiments designed to determine the extent to which conversion to this form can proceed. Jones and Bassett[4] and later Jones and Uhler[5] studied the effects of added dehydrating agents. They attributed the color changes to variations in the degree of hydration of the cobalt ion.

Brdicka's[6] work showed that the addition of anhydrous calcium chloride increases the activity of the cobalt ion. He employed Fajans'[7] theory of ion deformability to explain the color changes.

The object of the work herein reported was to compare the effects of added salts under identical conditions of solvent environment and to investigate the influence of the hydrating power of the cation of the added salt.

EXPERIMENTAL

Cobalt chloride, specified as "analytical reagent," was recrystallized three times for further purification. A fairly concentrated stock solution was prepared and standardized electrolytically.

Alkali and alkaline earth chlorides of "analyzed" grade were further purified by repeated recrystallizations. Constant boiling hydrochloric acid was prepared by the method of Hulett and Bonner.[8] Solutions containing a fixed concentration of cobalt chloride and varying concentrations of these salts and of hydrogen chloride were prepared with conductivity water.

The absorption spectra of the solutions were photographed with a large quartz spectrograph having a dispersion of 30A per mm at 5000A. The instrument was built by Dr. Thomas Poulter[9] and loaned for this investigation. A 150-watt Point-o-Lite lamp served as a light source.
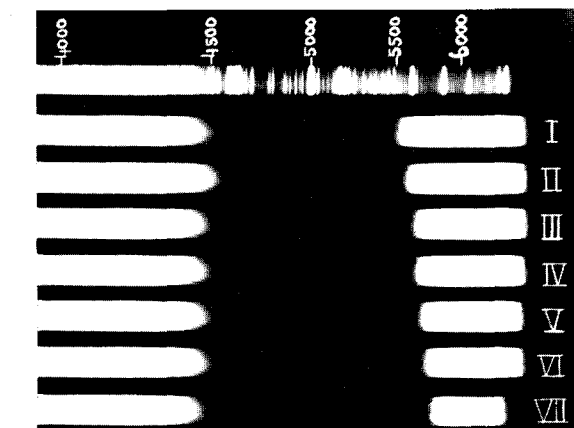

FIG. 1. Influence of salts (3.00 molal) on the absorption spectrum of $CoCl_2$ (0.250 molal). I, $CoCl_2$ alone; II. NH_4Cl; III, KCl; IV, $NaCl$; V, $LiCl$; VI, HCl; VII, $CaCl_2$.

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[1] Vogel, Ber. **11**, 913 (1878).
[2] Donnan and Bassett, J. Chem. Soc. **81**, 942 (1902).
[3] Macwalter and Barratt, J. Chem. Soc. **137**, 517–24 (1934).
[4] Jones and Bassett, Am. Chem. J. **34**, 290 (1905).
[5] Jones and Uhler, Am. Chem. J. **37**, 129, 207 (1907).
[6] Brdicka, Coll. Czechoslav. Chem. Comm. **2**, 545–58 (1930).
[7] Fajans and Joos, Physik. Zeits. **23**, 1 (1924).
[8] Hulett and Bonner, J. Am. Chem. Soc. **31**, 390 (1909).
[9] Chief scientist of the Second Byrd Expedition to Little America.

Eastman's spectrographic plates, type III-F, were used. These were developed in Eastman's solution, D-11, and fixed in Eastman's solution, F-I.

The cobalt chloride solutions were held in a Baly adjustable tube equipped with optical quartz ends. Adjustments in length with changes in concentration were made in such a way that the product of the thickness of the solution and the concentration of cobalt chloride per unit volume, remained constant.

Spectra of solutions containing equal concentrations (both 0.25 molal and 0.25 molar) of cobalt chloride and six different concentrations of each ammonium, potassium, sodium, lithium, hydrogen, and calcium chlorides were photographed. Each series of solutions was prepared both on the molal and on the molar bases. Also several series of spectrograms were obtained in which the effects of equimolal and equimolar concentrations of the added salts were compared. Only three of these series of spectrograms are included here.

DISCUSSION OF RESULTS

In all cases, absorption in the region from 4500A to 5500A increases with an increase in concentration of the added salt (spectrograms not shown). Comparing equal concentrations of different salts, it may be observed that increased absorption follows the order in which the solutions were photographed (Figs. 1–3). The effect is more pronounced in the solutions prepared on the molar basis than in those prepared on the molal basis. This is to be expected, for on the molar basis, the actual concentration of water molecules varies with the partial molal volume of the added salt. In solutions prepared on the molal basis, the ratio of water molecules to cobalt ions remains constant and the number of variables is reduced to one—the concentration of the added salt only. It is these spectrograms which yield data most applicable to the problem at hand.

Absorption increases with decrease in ionic volume of the added alkali cations. If the cation in hydrochloric acid is considered to be the proton, or hydrogen ion, it fits into the series. It has been shown[10, 11] that the degree of hydra-
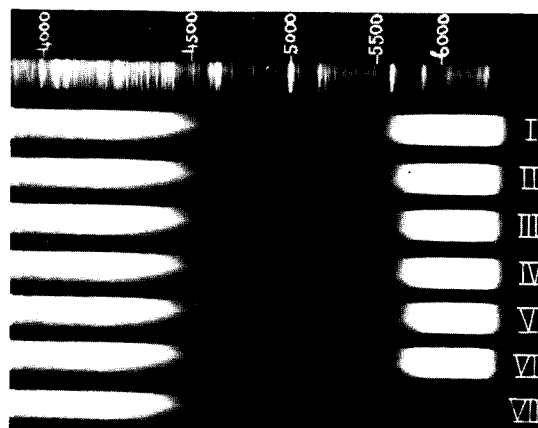

FIG. 2. Influence of salts (4.00 molal) on the absorption spectrum of $CoCl_2$ (0.250 molal). I, $CoCl_2$ alone; II, NH_4Cl; III, KCl; IV, NaCl; V, LiCl; VI, HCl; VII, $CaCl_2$.
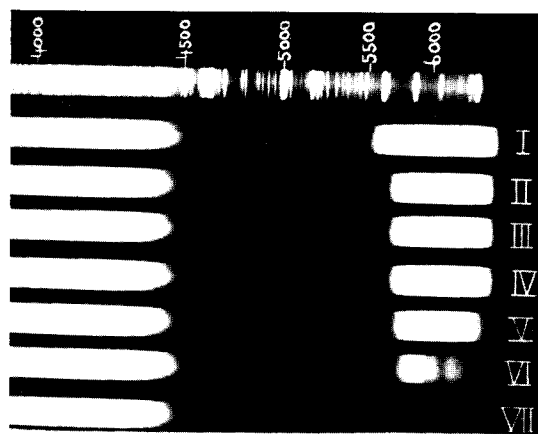

FIG. 3. Influence of salts (4.00 molar) on the absorption spectrum of $CoCl_2$ (0.250 molar). I, $CoCl_2$ alone; II, NH_4Cl; III, KCl; IV, NaCl; V, LiCl; VI, HCl; VII, $CaCl_2$.

tion of these cations varies in the same way. Thus, increased absorption of light and the consequent color changes accompany an increase in the degree of hydration of the cation of the added salt. This relationship is further established by the effects of the calcium ion, which has greater hydrating power than any of the alkalies. If the only absorbing mechanism[12] is the cobalt ion, one is forced to conclude that its change in character is associated with a decrease in the number of solvent molecules surrounding it. However, the explanation of this effect must involve some other factors.

[10] Jones and Pearce, Am. Chem. J. **38**, 683 (1907).
[11] Washburn, J. Am. Chem. Soc. **31**, 322 (1909).

[12] Vaillant, Comptes rendus **189**, 747 (1929); **190**, 170 (1930); **173**, 654 (1931).

The fact that equimolal high concentrations of added chlorides do not produce equal color changes serves to cast doubt upon the theory that complex ions, of the type $CoCl_4^{--}$ are formed. That such color changes could be due to deformation of the chloride ions[6] by strongly hydrating cations seems improbable, since pure concentrated solutions of aluminum chloride and of calcium chloride are colorless.

Absorption of energy in the visible region may be accomplished by the electrons[13] within the cobalt atom. The change in color of a dilute aqueous solution of cobalt chloride from red to blue, upon adding strongly hydrating cations, may be explained on this basis. In dilute solutions, the cobalt ion is completely hydrated. Solvent molecules are held tightly bound[14] and the solvent sheath prevents close approach of the cobalt and chloride ions. Electronic transitions in the unfilled third quantum group result from the

absorption of green wave-lengths and the solution is red. As strongly hydrating ions are added, they attract and orient solvent molecules. At high concentrations of the added salt, much of the solvent envelope about the cobalt ions is removed. Cobalt and chloride ions are then drawn more closely together by electrostatic attraction.

According to Lewis,[15] the strongly electronegative chloride ion tends to attract electrons of an ion near it. Thus, it is reasonable to assume that chloride ions distort the electronic system of the cobalt ion in such a way that the electrons in the third quantum group are capable of absorbing smaller quanta of energy. Hence, the yellow and red wave-lengths are absorbed and the solution becomes blue.

The blue color of concentrated solutions of pure cobalt chloride as well as of the anhydrous salt may also be explained in this way.

[13] Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Co., 1931), pp. 1533, 1544.
[14] Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

[15] Lewis, *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Co., 1923), p. 139.

Theory of Order for the Copper Gold Alloy System

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The theory of order and disorder, in the form used by Bragg and Williams, is extended to arbitrary composition of the constituent elements. The work is based upon the nearest neighbor interaction assumption of Bethe and the connection between the Bethe and Bragg-Williams theory is shown. In order to extend the Bragg-Williams theory to compositions other than 25 and 50 atomic percent, new definitions of order are developed. The results are presented in terms of phase diagrams and curves showing energy *vs.* temperature, specific heat *vs.* temperature and state order *vs.* temperature. These results are of importance in giving a general picture of the order-disorder transformation for a wide composition range. They are not in detailed accord with experiment due to the rather idealized picture underlying the nearest neighbor assumption.

I. THE NEAREST NEIGHBOR ASSUMPTION

1. Introduction

The phenomenon of order and superlattice formation in alloys is of an energetic nature, being governed by forces which tend to establish atoms in an orderly array. Several theories have been developed based on various assumptions regarding the relationships between the orderliness of the alloy and its energy.

The best known of these is probably that of Bragg and Williams.[1] They gave a quantitative significance to the concept of order by introducing the idea of "right" and "wrong" positions for the atoms. If an alloy in an imperfect state of order is compared with the perfectly ordered alloy, it will be apparent that a certain fraction of the atoms are missing from their "right" positions—those

[1] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934); **A151**, 540 (1935); **A152**, 231 (1935).