5. The interactions between chromyl chloride and the phosphorus trihalides are essentially oxidation-reduction processes as shown by the composition and properties of the compounds formed. The general equation for the reactions, namely,

$$2CrO_2Cl_2 + 3PX_3 \longrightarrow 2CrOCl.POX_3 + PX_3Cl_2,$$

indicates reduction of the hexavalent chromium compound to trivalent chromic compounds and the oxidation of trivalent phosphorus halides to pentavalent phosphorus compounds. Thus, on the basis of the established 2 : 3 ratio, the above equation reduced to its simplest term becomes

$$2Cr^{++++++} + 3P^{+++} \longrightarrow 2Cr^{+++} + 3P^{+++++}.$$

CINCINNATI, O.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE INFLUENCE OF THE POTASSIUM ION AND OF THE CALCIUM ION UPON THE FERRI-FERROCYANIDE POTENTIAL.

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OUTLINE.—1. Review of Previous Investigations. 2. Outline of Work Done and Results Attained. 3. Experimental Details and Calculation of Results. 4. Theoretical Considerations: (*a*) Significant Values of *n* and *k* for Ferricyanides and Ferrocyanides. (*b*) The Relation between the Activities and the Concentrations of the Ferricyanides and Ferrocyanides. 5. Summary.

Review of Previous Investigations.

The earliest measurements of the potential of the ferri-ferrocyanide[1] electrode were made by Schaum[2] and showed a dependence of the potential upon the concentration represented by Peters' modification of the Nernst formula

$$E_{obs.} = E_k + 0.0002\ T \log \frac{[\text{total ferricyanide}]}{[\text{total ferrocyanide}]}.$$

A little later (1902) Fredenhagen[3] obtained the same result.

However, the result announced by these investigators is not true in general but it is only true for a series of solutions in which the total ion concentration is constant. This was shown conclusively by Lewis and Sargent,[4] who made a rigorous test of the rule of mixtures by making up mixtures with constant potassium ion concentrations, but different ferri-ferrocyanide concentrations, and measuring their potentials. These

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[1] The term "ferri-ferrocyanide" is used in this paper to denote any mixture containing both potassium (or calcium) ferricyanide and potassium (or calcium) ferrocyanide with or without the chloride of the same metal.

[2] *Z. Elektrochem.*, **5**, 316 (1899); see also *Ibid.*, **9**, 406 (1903).

[3] *Z. anorg. Chem.*, **29**, 398 (1902).

[4] THIS JOURNAL, **31**, 355 (1909).

solutions were made by adding very small amounts of ferrocyanide and ferricyanide to solutions with relatively high concentrations of potassium chloride. The authors found that, as long as the K^+ ion concentration was kept constant, variations of the potential obtained by varying the ratio of the ferrocyanide to the ferricyanide concentration agreed to 0.1 millivolt with the differences calculated with the Nernst-Peters formula above.

Lewis and Sargent showed also that variations in K^+ ion concentration affect the ferri-ferrocyanide potentials very extensively, an increase in potassium ion concentration making the potential more positive. The amount of this change is much greater than the change of potential calculated from the change in the ratio of the concentrations of free ferricyanide to free ferrocyanide ions if the latter are calculated from conductivity ratios.

E. Mueller[1] has shown recently that the influence of the potassium ion upon the potential of mixtures with high concentrations of potassium ion is expressed by the following formula:

$$E_{\text{obs.}} = E_k + 0.0002\ T \log \frac{[\text{total ferri.}] \times [K^+]}{[\text{total ferro.}]}.$$

This relation Mueller found to be true for ferro-ferricyanide solutions which are from 0.2 to 1.0 *N* with respect to potassium chloride, but it is not true for more dilute solutions.

The foregoing presents the latest work upon the subject of this paper which has come to our notice.

Outline of Work Done and Results Attained.

In order to gain farther insight into the concentration relations in ferri-ferrocyanide mixtures, we prepared two series of mixtures and measured their specific conductivities, and their potentials against a standard electrode. In one series, the mixtures contained only potassium ferricyanide and potassium ferrocyanide, while in the other series the mixtures contained potassium chloride in addition to these salts. The concentrations of the two or three salts in the mixtures are given in Table II at the end of the next section of this paper. Both series begin with very dilute mixtures, and extend to moderately concentrated mixtures, and the relative proportions of the two or three salts are varied extensively. The experimental details of this work are presented in the next section of this paper, and the results of the measurements are given in Table II.

The calculation of the concentrations of the ions and of the un-ionized molecules in these mixtures was made under the assumption that intermediate ions are not formed, and that the degrees of ionization are given

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[1] *Z. physik. Chem.*, **88**, 46 (1914).

by the conductivity ratios of the salts. But before this could be done, it was necessary to determine the conductivity-concentration curves of potassium ferrocyanide and of potassium ferricyanide, and to obtain from these the ionic conductances of the ferrocyanide ion and of the ferricyanide ion. The values obtained for the latter were checked by the determinations from calcium ferrocyanide and calcium ferricyanide. The conductivity data for these salts are given in Table I at the end of the next section. All concentrations in this article for which the concentration units are not stated are expressed in milli-equivalents per liter!

With these conductivity data, the concentrations of the ions in the ferri-ferrocyanide mixtures were then calculated by a method which has been described by Sherrill[1] and others. The results of these calculations are given in Table II.

In order to determine whether or not the rule of "isohydric" mixtures holds with mixtures containing salts of the uni-trivalent and uni-quadrivalent types, the specific conductances of these mixtures were measured and compared with values calculated on the basis of these assumptions.

A comparison of the calculated with the observed conductances of these mixtures (see Table II, last two columns) reveals that for nineteen out of the twenty-eight mixtures these two values either agree very closely, or the calculated values are higher by less than 1%. In four other mixtures (Nos. 14, 17, 21, and 22) the calculated values are nearly 2% higher than the observed; and in Mixtures 9, 10, 23, 27, and 28 the calculated values are from 2 to 3% higher than the observed.

The observed conductances of Mixtures 1–8 and 13–22 inclusive are more dependable than the others because they were checked, not only with mixtures made from the same stock solutions, but also with mixtures made from different stock solutions. For ten of these eighteen mixtures, the calculated conductances exceed the observed by less than 0.5%; for four others, the calculated conductances exceed the observed by about 1%, and for the remaining four, the calculated values exceed the observed by a little less than 2%. The duplication with mixtures from different stock solutions served to eliminate several observed values which differed by more than 2% from the calculated values, and hence it is likely that similar duplication with Mixtures No. 9, 10, 23, 27, and 28 would reduce the differences between their calculated and observed conductances to less than 2%.

The agreement between the calculated and observed conductances of these mixtures is sufficiently close to justify the conclusion that the rule of mixtures holds for mixtures of salts of the uni-trivalent and uni-quadrivalent types.

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[1] THIS JOURNAL, 32, 741 (1910).

Since the difference between the potentials of the two ferri-ferrocyanide mixtures is much larger than the potential difference calculated from these "calculated" concentrations of the ferricyanide ion and ferrocyanide ion by means of the Nernst-Peters formula

$$E_{(25^\circ \text{C.})} = E_k + 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferrocy. ion}]},$$

and since it is known that the potential also depends upon the concentration of the potassium ion, the idea naturally presented itself to introduce in this formula, under the logarithm, the concentration of the potassium ion *raised* to a power, x, which is to be determined by trial. Thus modified, the formula has the form,

$$E_{\text{obs. } 25^\circ \text{C.}} = E_{k_1} + 0.0591 \log \frac{[\text{ferricy. ion}] \times [\text{K}^+]^x}{[\text{ferrocy. ion}]} \cdot \qquad (\text{I})$$

With the concentrations of the ferrocyanide, ferricyanide, and potassium ions expressed milliformal, it was found that values of x extending from 0.725 to 0.750 gave fairly constant values for E_{k_1}. The variations in the values of E_{k_1} obtained with different values of x extending from 0.6 to 0.8 are shown in Table IV. With $x = 0.725$ the maximum difference between individual E_{k_1} values is 4.3 millivolts; with $x = 0.75$ it is 4.4 millivolts; while with other values of x, the maximum differences between individual E_{k_1} values are much greater.

Concerning the choice of the value of x, we observe the following: the E_k values obtained with $x = 0.725$ or 0.750 show no *progression* with Σi either in the series of the mixtures without potassium chloride or in the series with it; and with all kinds of mixtures the different values show equal variations on both sides of the mean. The E_k values obtained with larger or smaller values of x differ from those obtained with $x = 0.725$ or 0.750 by the amount

$$dE_k = (0.725 \text{ or } 0.750 - x)\ 0.0591 \log [\text{K}^+]$$

and hence they present series of values progressing with Σi. It is evident that the attempt to use x values other than 0.725 or 0.750 together with a change in x proportionate to Σi and intended to eliminate the value of dE_k—that this attempt would give the same relation that a constant x would give. Hence x is considered to be constant and equal to 0.725 to 0.750.

The maximum variation of 4.3 millivolts, which the values of E_{k_1} corresponding to $x = 0.725$ present, is not large in comparison with the total range of 152 millivolts in the potentials of the mixtures, particularly in view of the fact that the compositions of the mixtures present a range of total potassium ion concentration (or Σi) extending from 7.85 to 395 milli-ions per liter.

In order to ascertain the nature of the causes which produce these variations in E_{k_1}, we should note that the mixtures which contain only ferricyanide and ferrocyanide (Nos. 1 to 12, inclusive) show variations in E_{k_1} of the same extent and kind as mixtures which contain these two salts in relatively small concentrations together with potassium chloride in relatively great concentrations (Nos. 13 to 20, inclusive).

An idea of the extent to which the contact potentials in these cells may affect the observed potentials can be obtained by a comparison of some of these. Since the equivalent conductance of the ferrocyanide ion at 25° is 111 mhos, that of the ferricyanide ion 93.2 mhos, and that of the potassium ion 74.8 mhos, it follows that the contact potential between a solution containing mainly potassium ferrocyanide and the solution of potassium chloride in the calomel electrode (as in Nos. 9 and 11) will be greater than the contact potential between a solution containing mainly potassium ferricyanide—but with the potassium ion of the same concentration as in the ferrocyanide solution—and the same calomel electrode (as in Nos. 10 and 12, respectively). These contact potentials act in such a sense as to *increase* the observed potentials of the cells, because the ferri-ferrocyanide poles are positive to the calomel electrode; and in accordance with these considerations, we find that the E_{k_1} value of No. 9 is 0.7 millivolt greater than that of No. 10, while that of No. 11 is 2.1 millivolts greater than that of No. 12. Again, the contact potential between the calomel electrode and any particular one of our solutions containing mainly potassium chloride should be less than that between the same calomel electrode and any of our ferri-ferrocyanide mixtures containing no potassium chloride but with the potassium ion of the same concentration as the particular "potassium chloride" solution selected: this is shown to be the case with Nos. 8 and 18 (difference 2.7 millivolts), Nos. 4 and 15 (difference 2.9 millivolts), Nos. 5, 16, and 22 (difference 2.2 millivolts), Nos. 7 and 17 (difference 0.4 millivolt). These observations indicate the amount of variation due to the contact potential, and they also indicate that the variations in the values of E_{k_1} are due largely, if not entirely, to the contact potential. In any case, the variations not thus accounted for do not exceed 2 millivolts, and they affect the two series of mixtures—*i. e.*, with and without potassium chloride—alike.

The average value of E_{k_1}—the normal potential—obtained with $x = 0.75$ is $+ 0.0526$ volt. With $x = 0.725$, E_{k_1} is equal to $+0.0554$. This is the potential of the ferro-ferricyanide electrode with all active components at unit concentrations, with this electrode measured against the "normal" calomel electrode, at 25°, and with a saturated potassium chloride solution between the two electrode liquids. Since in the general formula the expression under the logarithm contains two concentration factors in the numerator, but only one in the denominator, the numerical value obtained from the formula depends upon the units in which the molecular concentrations are expressed. The E_{k_1} values presented in this paper are obtained by expressing concentrations in millimols per liter; hence if they were expressed in mols per liter, the E_{k_1} value would be different by an amount equal to 0.0591 log 1000 = 0.1773 volt, and its value would be

$$E_{k_1} = +0.0526 + 0.1773 = +0.2299 \text{ volt, if } x = 0.75,$$

or

$$= +0.0554 + 0.1773 = +0.2327 \text{ volt, if } x = 0.725.$$

It should also be noted that this E_{k_1} value is, as it should be, different from the ordinary "normal" potential which is 0.4 volt, as given by Abegg, Auerbach and Luther.[1] The latter value rests upon the assumption that the ferrocyanide and ferricyanide ions alone affect or determine the potential. In reality, however, Abegg, Auerbach, and Luther's value is obtained only with a certain concentration of potassium ion, and hence is really not a *normal* potential.

Since the pole reaction in these ferri-ferrocyanide mixtures may also be expressed as follows:

$$K_3Fe(CN)_6 + K^+ + 1(-) = K_4Fe(CN)_6$$

it was to be expected that the potential may be expressed as a function of the un-ionized ferricyanide and ferrocyanide, together with some power of the potassium ion concentration.

It was found that the formula

$$E_{\text{obs. }25°} = E_{k_2} + 0.0591 \log \frac{[\text{K-ferricy.-U}] \times [K^+]^y}{[\text{K-ferrocy.-U}]} \qquad \text{(II)}$$

gives fairly constant E_{k_2} values when $y = 0.675$.

The "mean" values, obtained with various values of "y" and with the concentrations of the substances expressed "milli-formal" are presented in Table IV. The mean E_{k_2} value obtained with $y = 0.675$ is +0.0753 and the maximum difference between individual E_{k_2} values is 6 millivolts.

In order to throw further light upon the relation of the "cation" concentration upon the ferri-ferrocyanide potential, this work with the potassium salts was repeated with the corresponding calcium salts. Special experimental details concerning the preparation of these salts, etc., are given below, under a separate heading, together with other experimental details. The conductivity data for the separate calcium salts are given in Table I, and the data for the mixtures of calcium salts are given in Table III.

A glance at the last two columns in Table III reveals that the observed and the calculated specific conductivities of the mixtures of calcium salts agree fairly well with each other and thus corroborate the results obtained with the potassium salt mixtures.

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[1] *Abh. Bunsen Ges.*, No. 5 (1911).

The potentials of the calcium salt mixtures also corroborate the results obtained with potassium salt mixtures. Thus with the formula

$$E_{\text{obs. }25^\circ} = E_{k_3} + 0.0591 \log \frac{[\text{ferricy. ion}].[\text{Ca}^{++}]^z}{[\text{ferrocy. ion}]} \qquad \text{(III)}$$

a fairly constant set of E_k values is obtainable. The values of E_{k_3} calculated, with various values of z, by means of the data and measurements of the mixtures of calcium salts are given in Table IV. E_{k_3} values obtained with $z = 0.625$ have a mean value of $E_{k_3} = 0.0916$ and a maximum difference between individual E_{k_3} values equal to 1.7 millivolts only.

The formula

$$E_{\text{obs. }25^\circ} = E_{k_4} + 0.0591 \log \frac{[\text{Ca-ferricy.-U}].[\text{Ca}^{++}]^q}{[\text{Ca-ferrocy.-U}]} \qquad \text{(IV)}$$

gives fairly constant E_{k_4} values with $q = 0.575$; the mean E_{k_4} value is 0.1415 and the maximum difference between individual E_{k_1} values is 4.1 millivolts. Table IV shows the .different values of E_{k_4} calculated by assigning different values to q in the potential Formula IV.

This completes the presentation of the results obtained directly from the experiments.

Experimental Details and Calculations of Results.

A. Preparation of Solutions and Determination of Conductivities.—The details of the preparation of the different solutions and of the determinations of their conductivities are given under their respective headings in Notes 1 to 6 below, and the conductivity data are given in Table I.

Note 1. Potassium chloride: The values for the conductivities at 25° for this salt were taken from the tabulated results of Noyes and Falk[1] and are found in Table I. The salt which we used in our ferri-ferrocyanide *mixtures* was "C. P." stock recrystallized twice from conductivity water; the stock solutions were made up by carefully weighing out the required amount of the carefully dried salt and dissolving in conductivity water. The conductivity of our stock solution of potassium chloride was found to agree well with the data given by Noyes and Falk.

A Nernst conductivity vessel was used in all conductivity measurements; its capacity was determined with a freshly prepared 0.1 *N* potassium chloride solution, the specific conductance of which was taken as 0.01289 at 25°. The measurements were all made in a large water thermostat whose temperature remained constant at 25° to within 0.1°. Viscosity corrections were not applied to the results because we did not have accurate apparatus for this purpose.

Note 2. Potassium ferrocyanide: This salt was obtained pure by recrystallizing "C. P." stock twice from conductivity water. To avoid decomposition of the ferrocyanide by local overheating, hot saturated solutions were prepared by heating in a salt water bath. Stock solutions of known strength were made by accurately weighing out the carefully dried salt. Care was taken *not* to remove any of the water of crystallization of the ferrocyanide. In every case the strength of the stock solution was checked by means of titration with permanganate according to the method of de Haën.[2]

[1] This Journal, 34, 454 (1912).

[2] *Ann. Chem. Pharm.*, 90, 160 (1854).

The conductivities of these stock solutions of potassium ferrocyanide agreed well with previously published results.[1] The conductivity data for the higher concentrations of the potassium ferrocyanide as found in Table I were taken from measurements made in this laboratory.

Note 3. Potassium ferricyanide: This salt was prepared pure by recrystallizing "C. P." stock twice from conductivity water. The "standard" stock solutions were prepared by weighing out the carefully dried salts and checking the strength by reducing the ferricyanide in alkaline solution by means of ferrous sulfate to ferrocyanide, and then titrating with permanganate. The conductivities of the stock solutions prepared at various times were found to agree well with each other.

Note 4. Calcium chloride: The calcium chloride solutions were prepared by treating, in a calibrated volumetric flask, the required amounts of dry calcium carbonate (obtained by repeatedly washing freshly precipitated calcium carbonate) with the required amounts of hydrochloric acid of known strength. The solutions, after reaction, were boiled carefully to expel all carbon dioxide, and the solution diluted up to the mark with conductivity water. The strengths of these solutions were checked by means of the oxalate-permanganate titration and the silver chloride precipitation.

Note 5. Calcium ferrocyanide: This salt was prepared pure by recrystallizing "C. P." stock twice from conductivity water. The precaution for the prevention of local overheating as given in Note 2 was again observed. The salt was also prepared by treating the ether compound of hydroferrocyanic acid (in a flask with water) with an excess of purified calcium carbonate according to the method of Noyes and Johnston.[2] Solutions from both preparations of the salt gave the same conductivity. Stock solutions were prepared by weighing out the carefully dried salt, checking with the permanganate titration (here glacial acetic acid was used to acidify for the permanganate titration instead of sulfuric acid to avoid the formation of calcium sulfate).

Note 6. Calcium ferricyanide: This salt was prepared electrolytically from the purified calcium ferrocyanide. A concentrated solution of the purified calcium ferrocyanide was put into a clean porous cup and the cup placed in a glass jar containing a solution of purified potassium ferrocyanide. A platinum gauze anode and a mechanical stirrer extended into the porous cup. The cathode of platinum wire was placed into another porous cup filled with potassium ferricyanide solution in order to prevent the cathodic reduction product from reaching the anode cup. The current density employed was very low—not above 2 amperes per 100 sq. cm.—and the current was sent through the cell until a sample, tested with ferric chloride, gave no indication of ferrocyanide. The strength of the solution was determined by reducing the ferricyanide in alkaline solution by means of ferrous sulfate to ferrocyanide, and then titrating the latter with permanganate.

In order to obtain the conductivities at infinite dilution, two methods were used. In one, conductivities are plotted against concentrations and the curve extended until it cuts the conductivity axis: this point of intersection gives the conductivity at "zero" concentration. In the other—the method of Noyes and Coolidge[3]—$1/L$ is plotted against $(CL)^{n-1}$, and the value of n is taken so as to obtain a straight line: this line cuts the $1/L$ axis at the value $1/L_o$ (L_o being the equivalent conductivity at "zero" concentration). These two methods of determining

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[1] This Journal, 34, 454 (1912).

[2] *Ibid.*, 31, 987 (1909).

[3] *Pub. Carnegie Inst. Wash.*, No. 63 (1907).

L_o agreed well for all the salts used in this investigation with the exception of calcium ferricyanide. For this salt, the value of L_o obtained by extending the conductivity-concentration curve until it cuts the conductivity axis is 156, while the nearest approach to this value obtainable with the second method of determining L_o—plotting $1/L$ against $(CL)^{n-1}$—is 158.8. The value of n required to give this latter value of 158.8 is as high as 1.8; the value of n for potassium ferrocyanide, potassium ferricyanide, and calcium ferrocyanide which gave the *straight line*[1] were all the same, $n = 1.65$. Hence the value 156 for L_o was taken as the correct value in preference to the value 158.8.

The equivalent conductance of the ferrocyanide ion, $L_{(\text{ferrocy.})}$, obtained from L_o of calcium ferrocyanide by subtracting the equivalent conductance of the calcium ion, L_{Ca}, from the L_o value—is 110.0, while $L_{(\text{ferrocy.})}$ obtained from the L_o of potassium ferrocyanide is 110.5—which figures agree well with each other.

The equivalent conductance of the ferricyanide ion at 25° was found to be 93.2 as determined from the potassium ferricyanide data and 96 as determined from the calcium ferricyanide data. In the calculations of the conductivities of the mixture, the value of the equivalent conductance of the ferricyanide ion was taken as 93.2, because with this value

TABLE I.

Conductivities at 25° of the Salts Used in the Ferri-ferrocyanide Mixtures.

(Concentrations in milliequivalents per liter.)

	Conductivity of:					
Conc.	KCl.	$K_4Fe(CN)_6$.	$K_3Fe(CN)_6$.	$CaCl_2$.	$Ca_2Fe(CN)_6$.	$Ca_3[Fe(CN)_6]_2$.
0.0	150.60	185.00	168.00	135.80	171.00	156.00
0.5	....	....	162.90	....	112.30	138.80
1.0	....	....	160.20	130.20	105.10	126.60
2.0	146.55	160.10	157.60	128.50	89.40	114.80
5.0	143.95	146.90	149.90	123.20	67.10	101.00
10.0	141.40	135.35	141.70	120.40	57.70	88.80
20.0	138.65	123.30	134.20	115.30	49.30	82.15
50.0	133.65	108.30	121.40	111.30	41.85	72.45
100.0	129.00	98.20[2]	113.50	105.30	37.61	67.90
200.0	124.00	89.75[3]	107.20	99.25	35.63	64.61
500.0	118.80	81.00[4]	98.80	90.96	34.70	61.50
1000.0	117.40	77.20	93.60	88.08	33.86	57.74

[1] The n values for all these salts, determined by a method developed in this paper, are different from 1.65 and from each other; but they do not apply to solutions of very low concentrations .and hence they cannot be used for extrapolation to zero concentration in order to determine the L_o values. The "straight line" exterpolation method for determining L_o was the only one available to us, and the use of $n = 1.65$ in these L_o determinations has no connection with the use of other n values for higher concentrations.

[2] Repeated in this laboratory and found to agree with the data of Noyes and Falk.

[3] THIS JOURNAL, 34, 454 (1912).

[4] Concentration is 633 milliequivalents per liter.

the observed conductivities agreed fairly well with the calculated conductivities.

B. Potential Measurements.—The potential measurements of the different ferro-ferricyanide mixtures were made by means of an accurate potentiometer system, consisting of an extremely sensitive galvanometer of the D'Arsonval type, a Weston cell standardized by the Bureau of Standards at Washington, and a carefully prepared calomel electrode. This electrode was one of several which were found to remain constant to each other, and it was always kept in the thermostat, where all measurements were made. In the mixtures, gold electrodes are found to give more satisfactory results than platinum electrodes, which confirms the observations of Lewis[1] and of E. Mueller.[2] Since all mixtures were made up at a temperature slightly below the temperature of the bath, 25°, the

TABLE II.

Values of the Potentials and of the Specific Conductivities of the Potassium Ferri-ferrocyanide Mixtures (concs. in "milliformals" per liter).

$K_4Fe(CN)_6$.	$K_3Fe(CN)_6$.	KCl.	ΣK^+.	E_{obs}.	E_k calc. $x=0.750$.	E_k calc. $x=0.725$.	$Cond._{obs}$.	$Cond._{calc}$.
1.25	1.66	None	7.85	0.1066	0.0549	0.0562	0.00138	0.00137
2.50	3.33	None	14.60	0.1173	0.0525	0.0545	0.00237	0.00235
5.00	5.00	None	23.46	0.1212	0.0546	0.0566	0.00415	0.00415
10.00	10.00	None	43.20	0.1327	0.0538	0.0564	0.00765	0.00765
12.50	16.66	None	60.40	0.1469	0.0539	0.0564	0.01058	0.01058
20.00	20.00	None	80.00	0.1442	0.0526	0.0554	0.01414	0.01414
25.00	25.00	None	97.60	0.1466	0.0511	0.0540	0.01725	0.01729
50.00	50.00	None	181.90	0.1624	0.0541	0.0574	0.03203	0.03214
90.00	10.00	None	180.75	0.1052	0.0537	0.0570	0.03354	0.03250
10.00	90.00	None	183.24	0.2176	0.0530	0.0563	0.03189	0.03115
9.00	1.00	None	24.13	0.0656	0.0549	0.0570	0.00442	0.00443
1.00	9.00	None	22.66	0.1757	0.0528	0.0558	0.00392	0.00388
5.00	5.00	5	27.58	0.1247	0.0549	0.0571	0.00478	0.00478
5.00	5.00	10	31.67	0.1252	0.0526	0.0548	0.00527	0.00537
5.00	5.00	25	43.75	0.1300	0.0509	0.0533	0.00716	0.00716
5.00	5.00	50	64.25	0.1390	0.0517	0.0546	0.01010	0.01021
5.00	5.00	100	104.55	0.1498	0.0507	0.0534	0.01593	0.01617
5.00	5.00	200	183.20	0.1597	0.0514	0.0547	0.02750	0.02785
5.00	5.00	300	248.85	0.1671	0.0531	0.0567	0.03810	0.03852
5.00	5.00	400	332.39	0.1722	0.0535	0.0564	0.05015	0.05050
10.00	10.00	10	51.22	0.1335	0.0511	0.0536	0.00868	0.00881
10.00	10.00	25	63.00	0.1386	0.0517	0.0544	0.01036	0.01057
10.00	10.00	50	83.90	0.1430	0.0507	0.0536	0.01325	0.01353
10.00	10.00	100	122.59	0.1515	0.0510	0.0542	0.01942	0.01946
10.00	10.00	250	238.30	0.1673	0.0543	0.0576	0.03603	0.03654
10.00	10.00	400	349.00	0.1725	0.0520	0.0558	0.05290	0.05290
25.00	25.00	200	250.00	0.1658	0.0529	0.0555	0.03887	0.03996
25.00	25.00	400	395.00	0.1760	0.0531	0.0568	0.06045	0.06171

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[1] THIS JOURNAL, 31, 355 (1909).

[2] *Z. physik. Chem.*, **88**, 46 (1914).

potential of the mixture immediately after the preparation was slightly more positive than the final potential that it attained after 15 or 20 minutes, *i. e.*, when the mixture had attained the temperature of the bath.

TABLE III.

Values of the Potentials and of the Conductivities of the Calcium Ferro-Ferricyanide Mixtures (concs. in "milliformals" per liter).

$Ca_2Fe(CN)_6$.	$Ca_3[Fe(CN)_6]_2$.	$CaCl_2$.	ΣCa^{++}.	$E_{obs.}$	E_k ($z=0.625$).	Cond.$_{obs.}$	Cond.$_{calc.}$
1.00	1.00	None	2.95	0.1440	0.0917	0.000777	0.000770
2.50	2.50	None	5.25	0.1554	0.0923	0.001695	0.001652
5.00	5.00	None	9.45	0.1648	0.0918	0.003066	0.002971
10.00	10.00	None	17.50	0.1744	0.0916	0.005690	0.005491
25.00	25.00	None	43.25	0.1903	0.0913	0.016850	0.013620
5.00	5.00	5	13.15	0.1698	0.0914	0.003995	0.003960
5.00	5.00	10	16.90	0.1733	0.0909	0.004945	0.004967
5.00	5.00	50	46.00	0.1879	0.0907	0.012530	0.012545
5.00	5.00	100	79.50	0.1986	0.0924	0.021430	0.021890

TABLE IV.

E_k Values Corresponding to Different Values of x, y, z, and q in the Potential Formulas I to IV.

$$(a)\ E_{k_1} = E_{obs.} - 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferrocy. ion}]} - 0.0591\ (\log \Sigma i)(x).$$

Values of x	0.65	0.70	0.725	0.75	0.775	0.80
Mean value	0.0640	0.0582	0.0556	0.0528	0.0499	0.0472
Max. variation	0.0087	0.0052	0.0043	0.0044	0.0063	0.0082

$$(b)\ E_{k_2} = E_{obs.} - 0.0591 \log \frac{[\text{K-ferricy.-U}]}{[\text{K-ferrocy.-U}]} - 0.0591\ (\log \Sigma i)\ (y).$$

Values of y	0.600	0.625	0.650	0.675	0.700	0.750
Mean value	0.0866	0.0837	0.0817	0.0781	0.0753	0.0697
Max. variation	0.0095	0.0088	0.0083	0.0060	0.0082	0.0112

$$(c)\ E_{k_3} = E_{obs.} - 0.0591 \log \frac{[\text{ferricy. ion}]}{[\text{ferrocy. ion}]} - 0.0591\ (\log \Sigma i)\ (z).$$

Values of z	0.600	0.625	0.650	0.675	0.700	0.750
Mean value	0.0934	0.0916	0.0899	0.0881	0.0860	0.0826
Max. variation	0.0031	0.0017	0.0031	0.0056	0.0074	0.0099

$$(d)\ E_{k_4} = E_{obs.} - 0.0591 \log \frac{[\text{Ca-ferricy.-U}]}{[\text{Ca-ferrocy.-U}]} - 0.0591\ (\log \Sigma i)\ (q).$$

Values of q	0.50	0.550	0.575	0.60	0.625	0.65	0.675
Mean vlaue	0.1470	0.1436	0.1415	0.1396	0.1380	0.1361	0.1343
Max. variation	0.0060	0.0040	0.0041	0.0049	0.0067	0.0085	0.0102

The potentials of the potassium ferro-ferricyanide mixtures did not assume a steady value after having attained the temperature of the bath: most mixtures gave potential measurements that oscillated through a range of several tenths of a millivolt. In general the oscillation amounted to about three- or four-tenths of a millivolt—a few as high as a millivolt—and different mixtures of the same composition gave practically always the same range of oscillation within the same limits. The measurements were taken every ten minutes and the period of observation extended over two and one-half to three hours. The final potentials recorded in Tables II and III were an average of the entire series of measurements. Most mixtures were made up three times and few as many as four times. The calcium ferro-ferricyanide mixtures were extremely steady—at most, they showed much less oscillation than the potassium ferro-ferricyanide mixtures.

The numerical data and results of all this work have been presented in Tables I to IV.

Theoretical Considerations.

(*a*) **Significant Values of *n* and *k* for Ferricyanides and Ferrocyanides.**—In attempting to determine the *n* and *k* values of salts, we must neglect the range of extremely small concentrations and confine our consideration to the larger concentrations, because different causes operate in the two concentration ranges to produce variations in the values of *n* and *k*. This may be seen readily from the ionization function of Kraus and Bray[1] for uni-univalent salts:

$$\frac{[A^+][B^-]}{[AB]} = K + k\ [\Sigma i]^{2-n}$$

With very small values of Σi, the value of K forms a large part of the right side value, but with larger values of Σi, the value of K is negligible beside the term $k(\Sigma i)^{2-n}$. For the latter concentration range, the Kraus-Bray equation reduces to the Storch equation

$$\frac{[A^+][B^-]}{[AB]} = k[\Sigma i]^{2-n}$$

It is evident that the application of the Storch equation to ranges of very small concentrations will require values of *n* which increase rapidly as Σi decreases,[2] because this procedure amounts to neglecting the term K when its relative value is large enough to affect the result. It is evident that this cause of the *n* and *k* changes is essentially different from the cause or causes that bring about *n* and *k* changes in the ranges of higher concentrations.

If the causes of the changes in *n* and *k* which operate in the higher concentration ranges *be assumed* to continue *unimpaired* into very small concentration ranges, the values of *n* and *k* would tend toward certain final maximum values which we may obtain by exterpolation and which will be referred to in this paper as the *n* and *k* values at "zero concentration."

It should be noted that the formula

$$\frac{[C_i]^n}{[C_u]} = k,$$

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[1] Kraus and Bray, This Journal, **35**, 1315 (1913).

[2] Bates, *Ibid.*, **35**, 519 (1913).

shows that a lower value of either n or k will give a lower value for the other, even when all other quantities remain the same. Since the published values[1] of n for different concentration ranges correspond to different values of k, it is necessary to ascertain the nature of the change of *one* of these with concentration, while the other is kept *constant*. For this purpose, we have calculated from the data of Noyes and Falk the values of n for $C = 200$ milliequivalents, with k from the concentration range 1–20, and have obtained the following results: the n values at $C = 200$ thus obtained are *never greater* than those for lower concentrations, and for different salts, the "n-drops" vary considerably. Table V gives a number of values for illustration.

TABLE V.

Values of n with corresponding average values of k for certain concentration ranges;[2] and values of n for $C = 200$ obtained with *maximum* value of k (from range 0.1–20) showing rate of change of n with Σi (at 18°).

Salt.	Conc. range.	Corresponding n	and k	n for $C = 200$ with constant k.	Change of n with change in $\Sigma i = 150$.
KCl	0.1–20	1.48	47.12	1.450	0.030
	10–200	1.41	36.60		
NaCl	0.1–20	1.48	42.74	1.442	0.038
	10–200	1.41	36.00		
KNO_3	0.1–20	1.53	46.33	1.519	0.011
	10–200	1.51	44.60		
$NaNO_3$	0.1–20	1.50	42.42	1.481	0.019
	10–200	1.45	37.00		
$AgNO_3$	0.1–20	1.53	43.83	1.526	0.024
	10–200	1.52	43.80		
K_2SO_4	0.1–20	1.48	19.73	1.456	0.024
	10–200	1.42	15.83		
$CaCl_2$	0.1–20	1.43	19.72	1.402	0.028
	10–200	1.37	16.30		
$MgCl_2$	0.1–20	1.45	20.31	1.407	0.043
	10–200	1.38	17.50		
$Ca(NO_3)_2$	0.1–20	1.50	20.51	1.462	0.038
	10–200	1.44	18.10		
$Ba(NO_3)_2$	0.1–20	1.53	19.58	1.527	0.003
	10–200	1.53	19.60		
$Sr(NO_3)_2$	0.1–20	1.50	19.51	1.471	0.029
	10–200	1.46	18.20		
$MgSO_4$	0.1–20	1.60	6.30	1.564	0.036
	10–200	1.47	4.87		
$CuSO_4$	0.1–20	1.64	5.63	1.550	0.090
	10–200	1.47	3.80		

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[1] THIS JOURNAL, 34, 480 (1912).

[2] Conductivity data from Noyes and Falk, THIS JOURNAL, 34, 454 (1912). Attention should be called to the fact that some of these n values are different from those calculated by Noyes and Falk. Our calculations were made by assuming various values for one and calculating the other with the formula $(C_i)^n/(C_u) = k$, and then choosing that pair of values which gave the least variation.

In order to determine the n and k for any one salt, we should take its equivalent conductivities at three slightly different concentrations, and determine the values of n which come nearest to giving straight lines—or, in other words, we should apply to them the well-known procedure of A. A. Noyes[1] for determining the equivalent conductivity at infinite dilution. The closer the three points are taken together, the more accurate will be the determination of n (and hence of k); but for most salts, the changes in n and k with concentration are small enough to allow of drawing the straight line through points corresponding to a considerable range of concentrations as has been done by Noyes and Falk.[2]

But with ferricyanides and ferrocyanides, the n and k values vary so greatly[3] that the determination of the values of the latter would require the employment of three very slightly different concentrations. Instead of doing this, we made use of the following observation: it has been shown that when k is kept constant, the n values of all salts decrease with concentration; hence it follows that with n kept constant, the k values should *increase*. For those salts for which the "n-drops" (with constant k) are small, these rises in k will be very small—and hence inappreciable over a *limited* concentration range—but for ferricyanides and ferrocyanides, the k rise should be large. Hence we calculated by means of the ionization data of our most dilute solutions of ferricyanides and ferrocyanides the k values obtained with different n values, according to the formula

$$\frac{C_i^n}{C_u} = k,$$

and then selected for each salt those n values for the "n values at zero concentration" which gave series of moderately, but plainly rising k values. The "limits" which these k values appear to approach as the concentrations approach zero were taken as the "k values at zero concentration."

It should be realized that this relation between the changes in n and k values exists only with concentrations expressed in *whole* numbers. Since we have expressed concentrations in milliequivalents, the values used here are all greater than *one*.

In concluding this discussion of the n and k values, we present below the values for ferricyanides and ferrocyanides of the "n-drops" (with constant k) corresponding to a Σi range of 1 to 150 milliequivalents per liter. Attention should be called to the fact that all of these "n-drops" are

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[1] *Pub. Carnegie Inst. Wash.*, 63, 50.

[2] THIS JOURNAL, 34, 480 (1912).

[3] It was on this account that Johnson (THIS JOURNAL, 31, 987 (1909)), could not obtain a straight line graph through a number of points representing a considerable concentration range.

TABLE VI.

Values of "k" for various values of "n" in the dilution formula $\frac{[C_i]^n}{[C_u]} = k$.

(*a*)—Calcium Ferrocyanide:

Concentration.	n = 1.625.	n = 1.600.	n = 1.575.	n = 1.550.	n = 1.525.
5.0	0.998	0.983	0.965	0.946	0.932
10.0	1.102	1.069	1.038	1.008	0.977
10.0	1.232	1.171	1.121	1.072	0.922

The values obtained with the concentrations below 5.0 are irregular and hence have been omitted. The values obtained with n = 1.525 show no progression with concentration; those obtained with n = 1.625 show a great deal of progression; while the values obtained with n = 1.550, n = 1.575, and n = 1.600 show moderate amounts of progression, and hence these values of n have been accepted. The corresponding k values at zero concentration have been placed at 0.930, 0.945, and 0.960, respectively.

(*b*)—Potassium Ferrocyanide:

Concentration.	n = 1.700.	n = 1.679.	n = 1.650.	n = 1.600.
2.0	9.430	9.335	9.130	8.920
5.0	10.180	9.850	9.510	8.910
10.0	11.000	10.340	9.950	9.030
20.0	12.320	11.520	10.800	9.520

The values obtained with the concentrations below 2.0 are irregular and are hence omitted. The values of n = 1.700 show a great deal of progression; those for n = 1.600 show no progression; while the values for n = 1.675 and n = 1.650 show a moderate amount of progression, and hence these n values have been accepted. The coresponding k value at zero concentration have been placed at: k = 9.0 for n = 1.650, k = 9.15 for n = 1.675, and k = 9.30 for n = 1.700.

(*c*)—Calcium Ferricyanide:

Concentration.	n = 1.550.	n = 1.575.	n = 1.600.	n = 1.625.	n = 1.650.	n = 1.700.
2.0	3.34	3.36	3.40	3.43	3.46	3.52
5.0	3.52	3.63	3.74	3.85	3.97	4.21
10.0	3.49	3.58	3.80	3.01	4.08	4.52
20.0	4.06	4.31	4.56	4.85	5.16	5.87

The values obtained with the concentrations below 2.0 are irregular: the values for n = 1.550 show little or no progression, while the values for n = 1.700 show an excessive progression: hence the value n = 1.575, n = 1.600, n = 1.625, and n = 1.650, have been accepted. The corresponding k values at zero concentration have been placed at 3.30, 3.40, and 3.60, respectively.

(*d*)—Potassium Ferricyanide:

Concentration.	n = 1.650.	n = 1.700.	n = 1.725.	n = 1.750.	n = 1.775.
2.0	23.18	23.96	23.35	24.70	25.10
5.0	22.05	23.75	24.63	25.53	26.60
10.0	21.75	24.25	25.62	27.00	28.45
20.0	24.15	27.65	29.10	31.90	34.20

The values obtained with the concentrations below 2.0 are irregular; the values for n = 1.650 show no consistent progression, for n = 1.700 not quite enough progression, while for n = 1.775 the progression is excessive. The values n = 1.725 and n = 1.750 have been selected, and the corresponding k values at zero concentration have been placed at 22.0 and 23.0, respectively.

large, that the "n-drops" for the two potassium salts have the same value, and that those for the two calcium salts have the same value.

TABLE VII.

Rate of Change of n with Σi and a Comparison of the $(n - 1)$ Values with the Values of x, y, z and q for the Ferricyanides and Ferrocyanides of Potassium and Calcium.

Salt.	k value at "zero conc."	n value at "zero conc."	n values at approx. $\Sigma i = 150$ m. eq. per liter with k constant.	Change of n with change in Σi, 0.0 — 150.	$n-1$ values.	Values of x, y, z, and q.
$K_3Fe(CN)_6$........	22.00	1.725	C = 250 $\Sigma i = 156$	0.215	0.725	0.725
	23.00	1.750	1.510	0.233	0.750	0.750
			1.517			
$K_4Fe(CN)_6$........	9.00	1.650	C = 320 $\Sigma i = 149$	0.186	0.650	0 650
	9.15	1.675	1.464	0.205	0.675	0.675
	9.30	1.700	1.470	0.223	0.700	0.700
			1.473			
$Ca_3(Fe(CN_6))_2$.....	3.40	1.600	C = 400 $\Sigma i = 160$	0.280	0.600	0.600
	3.50	1.625	1.320	0.299	0.625	0.625
	3.60	1.650	1.326	0.320	0.650	0.650
			1.330			
$Ca_2Fe(CN)_6$.......	0.93	1.575	C = 750 $\Sigma i = 151$	0.290	0.550	0.575
	0.94	1.600	1.260	0.310	0.575	0.600
	0.96	1.625	1.265	0.355	0.600	0.625
			1.270			

It is evident from the last two columns that

$x + 1 = n$ for potassium ferricyanide at "zero" concentration.
$y + 1 = n$ for potassium ferrocyanide at "zero" concentration.
$z + 1 = n$ for calcium ferricyanide at "zero" concentration.
$z + 1 = n$ for calcium ferrocyanide at "zero" concentration.

(*b*) **The Relation between the Activities and the Concentrations of the Ferricyanides and Ferrocyanides.**—For uni-univalent salts, it may be considered fairly well established[1] that the values of $(2 - n)$ are the sum of the exponents of the Σi factors by which the concentrations must be multiplied or divided to obtain the activities. Thus, if $[Tl].[Cl].[1/\Sigma i]^a$ is the product of the activities of the ions of thallous chloride, and $[TlCl].[\Sigma i]^b$ is the activity of the un-ionized molecules, then

$$\frac{[Tl].[Cl]}{[TlCl]} = k[\Sigma i]^{a+b} = k[\Sigma i]^{2-n}$$

If, as we assume throughout this paper, polyionic salts form no intermediate ions and that the conductivity ratio gives the percentage of salt ionized into the ordinary simple ions, then the fact that, even in mixtures[2] the conductivity function for polyionic salts is of the form

$$\frac{[A^{++}].[B^{-}]}{[AB]} = k[\Sigma i]^{2-n}$$

instead of the form

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[1] Bray, THIS JOURNAL, **33**, 1673 (1911).

[2] Sherrill, *Ibid.*, **32**, 741 (1910).

$$\frac{[A^{++}].[B^{-}]^2}{[AB]} = k[\Sigma i]^{3-n}$$

This fact indicates that the relation between the concentrations and the activities of the components of polyvalent electrolytes (salts) includes another relation, different from the relation shown above for uni-univalent electrolytes, and which takes the place of—cancels—the higher powers otherwise required by the mass law. If this idea is correct, then the "cancelling" in the conductivity function for potassium ferrocyanide amounts to practically one [K+] more than in the conductivity function for potassium ferricyanide. Furthermore, we have

$$\frac{[\text{ferricy. ion}].[K^+]^{0.750}}{[\text{K-ferricy.-U}]} = 23 = \frac{[\text{act. ferricy. ion}].[\text{act. }K^+]^3}{[\text{act. K-ferricy.-U}]}$$

and

$$\frac{[\text{ferrocy. ion}].[K^+]^{0.675}}{[\text{K-ferrocy.-U}]} = 9.15 = \frac{[\text{act. ferrocy. ion}].[\text{act. }K^+]^4}{[\text{act. K-ferrocy.-U}]}.$$

Dividing *left*, *center*, and *right* of the first by the corresponding part of the last we obtain the following "concentration-activity relations from conductivities:"

$$\frac{\dfrac{[\text{ferricy. ion}]}{[\text{K-ferricy.-U}]}\cdot[K^+]^{0.075}}{\dfrac{[\text{ferrocy. ion}]}{[\text{K-ferrocy.-U}]}} = 2.4 = \frac{\dfrac{[\text{act. ferricy. ion}]}{[\text{act. K-ferricy.-U}]}}{\dfrac{[\text{act. ferrocy. ion}]}{[\text{act. K-ferrocy.-U}]}\cdot[\text{act. }K^+]}$$

Again, equating the expressions given by our *two* potential Formulas I and II for the potential for any particular ferri-ferrocyanide mixture, we obtain

$$E_{k_1} + 0.0591\log\frac{[\text{ferricy. ion}].[K^+]^{0.750}}{[\text{ferrocy. ion}]} = E_{k_2} + 0.0591\log\frac{[\text{K-ferricy.-U}].[K^+]^{0.675}}{[\text{K-ferrocy.-U}]}.$$

When numerical values are substituted for E_{k_1} (0.0526) and for E_{k_2} (0.0753), and this equation is simplified, it reduces to the *left-hand* equality in the concentration-activity relation above:

$$\frac{\dfrac{[\text{ferricy. ion}]}{[\text{K-ferricy.-U}]}\,[K^+]^{0.075}}{\dfrac{[\text{ferrocy. ion}]}{[\text{K-ferrocy.-U}]}} = 2.4$$

If we use activities in place of concentrations, we obtain

$$E_{k_1} + 0.0591\log\frac{[\text{act. ferricy. ion}]}{[\text{act. ferrocy. ion}]} =$$

$$E_{k_2} + 0.0591 \log \frac{[\text{act. K-ferricy.-U}][\text{act. K}^+]}{[\text{act. K-ferrocy.-U}]},$$

and this reduces to the *right-hand* equality in the concentration-activity relation above. Hence these two equations give us the same "concentration-activity relations" as that obtained above from the conductivity functions.

This relation shows that for all values of Σi—

$$x - y = n_i - n_0$$

because x and y are constant, and n_i and n_0 decrease equally with Σi. Since these four quantities are determined from *totally* independent data, this result shows that the "concentration-activity" relation of each component is the same in the conductivity functions as in the potential function.

It appears to us that the exponent of $[K^+]$—*i. e.*, $x - y$ or 0.075—is the *sum* of the different powers of $[K^+]$ which give the factors by which the different concentrations in the concentration must be multiplied to make them equal to the activities of the respective substances—as was illustrated with the thallous chloride at the beginning of this section. Seen in this light, the factor $[K^+]^{0.750}$ under the logarithm in our potential Formula I

$$\frac{[\text{Ferricy. ion}].[K^+]^{0.750}}{[\text{ferrocy. ion}]}$$

has merely a numerical significance: it is the factor by which the concentration ratio

$$\frac{[\text{ferricy. ion}]}{[\text{ferrocy. ion}]}$$

must be multiplied to make it equal to the activity ratio

$$\frac{[\text{act. ferricy. ion}]}{[\text{act. ferrocy. ion}]};$$

and the factor $[1/[K^+]^{0.325}]$ in our potential Formula II—

$$\frac{[\text{K-ferricy.-U}].[K^+]}{[\text{K-ferrocy.-U}]} \cdot \frac{[1]}{[K^+]^{0.325}}$$

serves the corresponding purpose. Evidently the activity of the ferrocyanide ion increases more with Σi than that of the ferricyanide ion; while for the un-ionized molecules the reverse is true.

It is rather surprising that x and y are constant while the similar exponent n varies with Σi. Perhaps the constancy of x is due to the chemical similarity between the ferricyanide ion and the ferrocyanide ion on account of which any "secondary" changes (with Σi) in the concentration-activity relation of one is undergone to an equal extent by the other; and since the ratio of these ions appears in the potential formula, such secondary effects would "cancel" out. In the same way, the constancy of the other exponents y, z, and q might be due to the chemical similarity of the other pairs of components concerned.

Finally, attention should be called to the fact that although

$$\frac{[\text{ferricy. ion}].[\text{K}^+]^{n-1}}{[\text{K-ferricy.-U}]} = k,$$

yet this relation cannot be used to substitute [K-ferricy.-U] for [ferricy. ion].$[\text{K}^+]^x$, because x is equal to the *maximum* value of n_i *only*, and not to the lower values of n_i corresponding to larger values of Σi.

Summary.

1. Conductivity measurements were made on solutions of potassium ferrocyanide and potassium ferricyanide, on solutions of mixtures of these and on mixtures of these with potassium chloride. The results were compared with results calculated by means of the rule of mixtures, and a fair degree of agreement was obtained.

2. Conductivity measurements were made on the corresponding calcium salts and on corresponding mixtures of these—with practically the same agreement between the observed and the calculated results.

3. The potentials of all these mixtures were measured against the "normal" calomel electrode.

4. The constituent ions and un-ionized molecules in all these mixtures were calculated on the assumption that intermediate ions are absent. The following empiric formulas were found to represent the dependence of the potentials upon the constituents of the mixtures through a K^+ range of 10 to 400 milliequivalents per liter:

$$E_{\text{obs. } 25^\circ} = E_{k_1} + 0.0591 \log \frac{[\text{ferricy. ion}][\text{K}^+]^{0.75}}{[\text{ferrocy. ion}]}$$

and

$$E_{\text{obs. } 25^\circ} = E_{k_2} + 0.0591 \log \frac{[\text{K-ferricy.-U}][\text{K}^+]^{0.675}}{[\text{K-ferrocy.-U}]}$$

Corresponding formulas were found to hold for the calcium salts.

5. A new method was presented for deriving significant values of n and k for such salts as ferricyanides and ferrocyanides, for which these values very greatly with the concentration. It was shown that the n values of the two potassium salts change equally with Σi. The same is true for the calcium salts. It was found that the "maximum" values of n (*i. e.*, the limits they approach with decreasing Σi) bear a simple numerical relation to the exponents of $[\text{K}^+]$—or of $[\text{Ca}^{++}]$—in the potential formulas above.

6. It was shown that certain of these observed relations are necessary consequences of the assumptions that the concentration-activity relation

of each component in the conductivity functions is the same as in the potential functions.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STANFORD UNIVERSITY.]

THE BASIC COPPER SULFATES.

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Introductory.

In connection with some investigations on the genesis of copper ores, the problem of the formation and character of Brochantite or native basic copper sulfate comes under consideration. The analyses of this mineral give widely varying results, so divergent in fact as to indicate the probability that the substance is not of fixed composition. It was decided to attack the whole problem from the purely chemical side and the first results of the investigation are contained in this paper.

In looking over the literature on the basic copper sulfates one is struck at once by the large number of such compounds described. In the Gmelin-Kraut "Handbuch" some thirty-five are described as presumably definite compounds. These supposed compounds vary between the limits, $10CuO.SO_3$ and $2CuO.SO_3$, with varying amounts of water. In some cases, salts, which differ from one another only in water content and this to only a very small degree, are given as distinct individuals. For example, one finds on record $4CuO.SO_3.3H_2O$ and $4CuO.SO_3.3^1/_2H_2O$. Five different formulas are given for salts supposed to be identical with natural Brochantite, namely: $4CuO.SO_3.3H_2O$; $7CuO.2SO_3.5H_2O$; $7CuO.2SO_3.6H_2O$; $3CuO.SO_3.2H_2O$; and $3CuO.SO_3.3H_2O$.

It seemed, on the face of it, to be highly improbable that such a large number of definite individuals of this class should exist, and good grounds for doubt are to be found by examination of the methods of preparation which have been used. Without going into detail concerning these methods, they may be fairly satisfactorily summarized under three heads:

1. Heating of copper sulfate solutions.
2. Precipitation from copper sulfate solutions by means of alkaline reagents such as sodium, potassium, calcium,[2] and ammonium hydroxides and carbonates, and in some cases by zinc oxide, as well as by acetates of the alkali metals.
3. Dilution of ammoniacal solutions of copper sulfate with water.

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[1] Abstract of a thesis presented by Allen Edwin Stearn to the faculty of Stanford University, in partial fulfilment of the requirements of the degree of Master of Arts, May, 1916.

[2] Many salts are described by Pickering as a result of his studies of the Bordeaux mixture.