165. *Diffusion Potentials and Mobilities of Multivalent Ions : Potassium Ferricyanide and Ferrocyanide.*

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The potentials, E_d, at various kinds of liquid junction between solutions of potassium sulphate, potassium ferricyanide and ferrocyanide, severally, have been determined by various methods. These potentials are proportional to log C_I/C_{II}, C_I and C_{II} being the concentrations. When extrapolated to zero concentration, the E_d values for potassium ferri- and ferro-cyanide are nearly equal, and the transport numbers t_- and mobilities l_- are in good agreement with those determined by conductivity. It is confirmed that the equivalent mobilities $_0l_-$ of $\frac{1}{4}[Fe(CN)_6]^{4-}$ and $\frac{1}{3}[Fe(CN)_6]^{3-}$ are in the ratio $1.11 : 1$. In solutions of higher concentration, the E_d values for the two salts diverge and are so related that the transport numbers of the two salts become equal when the concentration is $0.1N$; beyond this, the value for the ferrocyanide probably falls below that for the ferricyanide. The data are interpreted on the assumption that the only ions present are the potassium and the ferro- or ferri-cyanogen. Calculations based on the existence of an intermediate ion, *e.g.*, $[KFe(CN)_6]^{3-}$, although satisfactorily explaining the t_- and λ values, do not accord so well with the observed diffusion potentials.

Proportionality between Ion Mobilities and Charges.—It follows from the usual representation of ionic motions by the equation based on Stokes's law that, all other conditions being equal, the equivalent ionic mobility of the multivalent ion will be proportional to the total charge, and the mobility of the ion itself to the square of the charge. The difficulty of proving this proposition depends partly upon the fact that only in very special cases are the conditions equal. Stokes's law can probably only be regarded as valid for spheres of radius $>10^{-6}$ cm., and most simple ions of low molecular weight are smaller than this. It is usually considered that ions of virtually the same structure, *e.g.*, the phosphate and the hydrogen phosphate ions, will obey the same modified form of Stokes's law and thus be comparable; and actually only such ions have been compared.

The conductivities of various alkali and ammonium phosphates, and the distribution of ammonia between the aqueous phases and chloroform, were used to determine concentrations and eventually mobilities of the participating ions, as well as the first and the second dissociation constant of phosphoric acid, the third being less easy to define by conductivity methods. The limiting conductances were :

$H_2PO_4^{1-}$	HPO_4^{2-}	PO_4^{3-}	$P_2O_7^{4-}$
26.4 ± 1.0	106.8 ± 2	205.0 ± 30	325.6 ± 10
	$\frac{1}{2} = 53.4$	$\frac{1}{3} = 69.0$	$\frac{1}{4} = 81.4$
Factor	2.02	2.60	3.08

The factors representing the ratios of increase of mobility due to increased charge progressively depart from the theoretical values, 2, 3, and 4.

The fourth hydrogen ion of pyrophosphoric acid is even less dissociated than the third of orthophosphoric acid, and therefore the correction for hydrolysis, *e.g.*, of sodium pyrophosphate is even greater (a $0.0003M$-solution is 7% hydrolysed; Abbott and Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 729).

A greater choice of anions is afforded by polycarboxylic acids. For instance, the conductivities of the penta- and tetra-sodium salts of benzenepentacarboxylic acid were determined at 25° by Noyes and Lombard (*ibid.*, 1911, **33**, 1423). Ionic conductances of $C_{11}HO_{10}^{5-}$ and $C_{11}H_2O_{10}^{4-}$ were 496 and 332 respectively, ratio 1.49; whereas the theoretical ratio $5^2/4^2$ is 1.56. The first dissociation of the free acid is practically complete at a concentration of 6 millimols. per 1000 g. of water.

Essential material for an investigation of this subject is furnished by highly dissociated salts of tervalent and quadrivalent strong acids. The ferro- and ferri-cyanides fulfil these conditions, and possess the further advantage that their conductivity data are almost completely available.

Symbols used are those given in the Report of the Joint Committee of the Physical Society, the Faraday Society, the Chemical Society and British Chemical Abstracts, unless otherwise stated. For the equivalent ionic conductances or ionic mobilities, l_- and l_+, there are substituted sometimes (*i.e.*, in ratio terms from which F' cancels) the velocities u and v; t_+ and t_- denote the transport numbers of cation and anion. $E_{I \to II}$ is the diffusion potential between solutions having concentrations C_I and C_{II} ($C_I > C_{II}$) and is taken as positive when side I is positive to II.

A selection of the equations applicable to the present cases is as follows :

$$t_+ = l_+/(l_+ + l_-), \; t_- = l_-/(l_+ + l_-) \text{ or } v/(u + v) \quad \ldots \ldots \ldots (1)$$

or, in case several kinds of ions are present :

$$t_- = \Sigma v_i C_i/(\Sigma u_i C_i + \Sigma v_i C_i) \quad \ldots \ldots \ldots \ldots (2)$$

The change of t with concentration is given by an equation derived from that of Onsager by Hartley and Donaldson (*Trans. Faraday Soc.*, 1937, **33**, 457) *viz.*,

$$\mathrm{d}t_-/(\mathrm{d}\sqrt{C}) = (21\cdot14/\lambda)(z_-t_+ - z_+t_-)\sqrt{z_+ + z_-} \text{ as } C \to 0 \quad \ldots \ldots \quad (3)$$

The diffusion potentials are given by the general equation

$$E_{\mathrm{I}\to\mathrm{II}} = \text{constant} \times T\Big(\sum_{\mathrm{I}}\frac{t_-}{z_-} - \sum\frac{t_+}{z_+}\Big)\log\frac{a_{\mathrm{I}}}{a_{\mathrm{II}}} = 0\cdot0591\frac{z_+v - z_-u}{z_+z_-(u+v)}\log\frac{a_{\mathrm{I}}}{a_{\mathrm{II}}} \quad \ldots \quad (4)$$

in which the a's may be the activities determined by various methods, but in the present work are usually concentrations C expressed in g.-equiv./l. The second part refers to two kinds of ion of valencies, z_+ and z_-.

If n_+, n_-, and n are the numbers of cations, anions, and ions of both kinds, respectively, produced by the dissociation of 1 mol. of the salt, then the relation between the transport number factor $\mathrm{f}(u, v, z)$ or $\mathrm{f}(t_-, z)$ and the transport number t_- is

$$\mathrm{f}(t_-, z) = (t_- n/n_+ - 1)/z_+ \quad \ldots \ldots \ldots \ldots \quad (5)$$

In the electrolytes under consideration, $z_+ = 1$ and $n = z_- + 1$, also $n_+ = z_-$. Therefore

$$\mathrm{f}(t_-, z) = t_-(z_- + 1)/z_- - 1 \quad \ldots \ldots \ldots \ldots \quad (6)$$

in which the subscripts may be omitted from z.

In all cases where $z_- = 2, 3,$ or 4, $\mathrm{f}(t_-, z)$ is negative, and therefore $E_{\mathrm{I}\to\mathrm{II}}$ is negative, for although v may be greater than u, it is never greater than or equal to zu [equation (4)].

EXPERIMENTAL.

Liquid junctions of various types were measured in symmetrical chains or combinations of solutions contained in specimen tubes or salt-bridges and terminating in symmetrical half-cells which were the saturated (more rarely, N) potassium chloride–calomel–mercury type. These were connected by salt-bridges of the same potassium chloride solutions with guard tubes Ia and IIa, then came tubes I and II, between which was the liquid junction (broken line). Elimination of diffusion potentials by saturated potassium chloride salt-bridges is denoted by double lines as usual :

$$\text{Hg, HgCl, KCl}\,||\,\text{KCl}\,||\,\text{Ia}\,|\,\text{I}\,\vdots\,\text{II}\,|\,\text{IIa}\,||\,\text{KCl, HgCl, Hg}$$
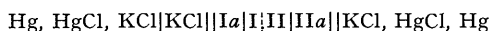
The equality of the electrodes was tested occasionally by connecting them directly, and that of the whole combination by substituting a saturated potassium chloride salt-bridge for the liquid junction. This does not, of course, reveal the existence or otherwise of a *P.D.* between saturated potassium chloride and Ia, which was, however, investigated by a special method described below.

The apparatus for static junctions was set up in an air thermostat. A double-walled, copper water-bath (dry) was heated at the bottom and sides by resistance elements, the current being controlled by a vacuum switch and bimetallic spiral. The air in the box was stirred by a fan inserted through the roof. Temperature between the walls was auto-regulated over a small range round 25°. During an experiment, it was hand-regulated between about 24° and 26°, and the temperature of the enclosed liquids was also maintained at $25° \pm 1°$.

The Liquid Junctions : Types of Apparatus.—Conditions for forming satisfactory liquid junctions have been discussed by Guggenheim (*J. Amer. Chem. Soc.*, 1930, **52**, 1315), Guggenheim and Unmack (*Kgl. Danske Videnskab. Selskab. Math.-fys. Meddelelser*, **x**, 8, 1930), and many previous investigators. Free-diffusion and continuous-mixture junctions were compared. In the former type the most important requisite for reproducibility is cylindrical symmetry within a tube. This was realised by drawing a solution up into the tube, which usually gave results reproducible to a few tenths of a millivolt in the case of the uni-univalent electrolytes investigated. A method which is said to give the best reproducibility is to run in the more concentrated solution I below a tap of the same bore as the tube, to close the tap, wash out the space above it, and then pipette in solution II. Satisfactory static junctions were obtained in the present work by preparing a solution bridge of II, one end of which was lightly plugged with cotton-wool or glass-wool, and immersing the two limbs slowly and uniformly in two tubes containing solutions I and II, the levels of which had been carefully adjusted so that the junction rose for a short distance. Potentials were established almost at once ; usually they remained constant for hours with the higher concentrations, or faded out in $\frac{1}{2}$ hour with the very low concentrations. It is well known that potentials of the C I, C II type are steadier than any other kind, and are mostly independent of the kind of junction (free-diffusion or continuous mixture) ; but in the case of the present unsymmetrical salts, variations in the static junctions are sometimes found, and these may depend on the degree to which the junctions at the moment of setting up approximate to one or other of these two types. If so, these variations certainly persist in any one experiment. For these and other reasons, it was considered desirable to carry out parallel experiments with flowing junctions.

Apparatus for Flowing Junctions.—The apparatus of Ferguson, Van Lente, and Hitchens (*J. Amer. Chem. Soc.*, 1933, **54**, 1285) consists of a very large three-way tap, the bore of which is the same as that of the inlet tubes of the two solutions and the outlet tube containing the liquid junction. The inlet tubes dip into two reservoirs containing solutions I and II at the same level. Tube I is first filled, above the tap, which is then turned, putting into communication solution II, which washes out the upper part. After adjustment of the reservoirs, the tap is turned back, establishing the junction without disturbance. On opening the outlet, a liquid junction is formed. Thus, either type of junction can be established at will, and can be preserved for long periods. This apparatus gives excellent results and requires only moderate quantities of solution. It is not very convenient for use in a thermostat.

Another form is that due to Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641, 698). The graduated reservoirs, side tubes, and outlet tube form one piece of robust construction, suitable for immersion in a thermostat. Solutions I and II are separated initially by a rubber stopper carried on a vertical glass rod. The stopper is first pressed down on to an accurately formed constriction. After the reservoirs have been levelled, the stopper is slowly raised and a static junction is established. This is converted into a flowing one by gradually opening the outflow tube, so that about 1 drop falls in 2—5 seconds. By this means static and flowing junctions can be measured at will. In the present series they were identical. As in the preceding form of apparatus, if the junction has been badly made or become mixed, it usually cannot be restored without emptying and refilling the apparatus. It also requires a large volume of solution,

which is somewhat reduced, however, by placing ballasted tubes in the reservoirs. Probably on account of its great area, this is the most reliable and reproducible of all liquid junctions, and is especially suited to pairs of solutions with a considerable difference of concentration, but less suited to very dilute solutions. Occasional high results, noticed in the static junctions, do not occur. On the other hand, potentials may be too low on account of mixing at the large surface, and soon fall when this becomes static, to rise again when the flow is resumed at the minimum rate mentioned above.

Roberts and Fenwick's junction (*ibid.*, 1927, **49**, 2787) is formed by allowing films of solutions I and II to stream past the opposite sides of a hole of about 1 mm. diameter, pierced in a vertical sheet of mica. The streams are directed down channels in the paraffined surface so as to form drops which must fall at about the same speed from separate points. This method requires delicate manipulation, and the directions given must be carefully observed. There are several sources of error and the apparatus is capable of improvement. Some satisfactory results, however, were obtained, which have some value as confirming those gained by the other methods. The flowing junctions, except that of Scatchard, were not thermostatically controlled, but were at room temperature, 16—20°.

Salt Solutions.—Potassium sulphate solutions were made from the " AnalaR " salt, and measurements carried out as above. Potentials were steady.

Potassium ferricyanide solutions were made from the " A.R." salt in good distilled water, the higher dilutions with conductivity water. On account of their instability, solutions should not be too old, but storage for several weeks in the dark does not affect the potentials. Solutions of about M/30-concentration show a slight precipitate, resembling ferric hydroxide, on long keeping, but this was absent from more concentrated or more dilute solutions. This is probably produced as a further stage of the first hydrolysis: $[Fe(CN)_6]^{3-} \rightarrow [Fe(OH)(CN)_5]^{3-} + HCN$. If the first stage is reversible, it might account for the uncertainty in potentials referred to below. Concentrations were sub-multiples of M/3 = 1·0N, and usually of M/30, the lowest being M/3000. Concentration ratios were usually 10/1, but sometimes 5/1, 20/1, or 50/1; the results usually showed a satisfactory agreement with the logarithmic law, and also suggested that, for purposes of computation, concentrations rather than activities should be used. One particular range, M/30—M/300, gave results which were less constant and more influenced by change of apparatus than any other pair. However, the apparatus with wide junction (Scatchard) gave a very steady 17 mv., which was taken as the most probable value.

Potassium ferrocyanide solutions were made from a good commercial salt which had been checked by analysis, and also from " A.R." reagent. They were made with distilled water, and in the higher dilutions with conductivity water. Concentrations were M/8 and M/20, but chiefly M/40 (=0·1N) and sub-multiples, the lowest being M/4000. Ratios of 10/1, 5/1, 20/1, and 50/1 were used, and the logarithmic law of concentrations was confirmed.

Potassium ferrocyanide is slightly hydrolysed in solution. When freshly made, solutions are neutral (to neutral-red), but in about 15 minutes they become alkaline (to phenolphthalein) (Kolthoff, *Z. anorg. Chem.*, 1920, **110**, 143). The hydroxyl-ion concentration corresponding to each solution may be estimated, from the fourth dissociation constant ($-\log K_4 = 4·237$ at C 20·1; Kolthoff and Tomsicek, *J. Physical Chem.*, 1935, **39**, 955) and pK_w at 18° = 14·27, to be 3×10^{-6}. In any case, this concentration is of a lower order than those of the other ions.

An M/40-solution which had been kept stoppered for some months gave a decided pink reaction with saturated phenolphthalein solution, but solutions of M/80 or lower concentration showed no colour.

Test for an Extra Diffusion Potential.—Attention has been directed above to the possibility of a diffusion potential at the junction between a saturated potassium chloride salt bridge and solution I when this is of the order of 0·1N or more. An attempt was made to evaluate this as follows. Potential differences were measured between smooth platinum electrodes, which function as oxidation–reduction electrodes in solution I, and the saturated calomel electrode. These were then compared with the values calculated from the single potentials of the half-cells.

Kolthoff and Tomsicek (*loc. cit.*) measured the potentials between a quinhydrone electrode in 0·01N-hydrochloric acid plus 0·09N-potassium chloride (paH * = 2·075, and therefore E_H = 576·4 mv.) against a ferri–ferro-cyanide (10 : 1) oxidation–reduction electrode. The value of E (total) was 102·0 mv. (quinhydrone positive), and therefore E_H of the complex cyanide half was 474·4 mv. The corresponding measurement with a ferro–ferri-cyanide (10 : 1) electrode was 208·8 mv.; E_H = 357·6. Subtraction of the single potential of the saturated calomel electrode, 246 mv. at 25°, gives 228·4 and 111·6 mv. respectively for the potentials against calomel (negative).

Single potentials of the calomel electrode used were checked against quinhydrone in standard acetate at 18°. Mean values were (i) 186·3, (ii) 186·0 mv. (Calc.: 186·4). The potentials of smooth platinum electrodes in solutions with the above two ratios of the two cyanides against saturated calomel electrodes at 25° were 224 and 112 mv., respectively. Since the foregoing theoretical potentials are calculated as differences between different electrodes measured independently and probably with different technique, the agreement is satisfactory. A small initial potential E' is, however, indicated between a potassium ferricyanide solution I (positive) and saturated potassium chloride. As this opposes the liquid-junction potential $E_{I \rightarrow II}$ a small positive correction may be due, but it seems better not to introduce this, since it is probably temporary and less important than the uncertainties attributed to reversible hydrolysis with local production of a less mobile ion, $[Fe(OH)(CN)_5]^{3-}$.

Measurements on Potassium Sulphate.—Methods of determining transport numbers and their variation with concentration are well exemplified by potassium sulphate, and the diffusion potentials of this standard substance were therefore added to the data.

Conductivities over a wide range of concentrations are recorded in " International Critical Tables " and a few values at high dilutions are given by Hartley and Donaldson (*loc. cit.*), who also determined the transport numbers by the method of moving boundaries; $_0\lambda$ is 154·3, and this when combined with $_0l_+(K^+)$ = 73·5 gives $_0l_-(\frac{1}{2}SO_4^{--})$ = 80·8 and t_- = 0·523 (MacInnes, Longsworth, and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 2738), or if $_0l_+$ is taken as 74·8 and $_0l_-$ as 80·0, t_- = 0·517 (Noyes and Falk, *ibid.*, 1911, **33**, 1436). The former value is in perfect agreement with that extrapolated from the experimental values of t_- (*a*) as obtained by the moving-boundary method, which were also compared with t_-, and (*b*) as calculated by the modified Onsager equation (3). In this calculation, $_0t_-$ = 0·523 and $_0\lambda$ = 154·3 have been used.

C, g.-equiv./l.	0·0	0·01	0·02	0·05	0·10
t, exptl.	0·523 (extrapol.)	0·517	0·515	0·513	0·511
f(t_-, z)	$-0·215_5$	0·225		0·23	
t (Onsager)		0·513		0·50	
f(t_-, z) (Onsager)		$-0·23$		$-0·25$	

Diffusion potentials are calculated from these data for the range 0·10—0·01 by means of the equation $E = f(t_-, z) \times 59$, in which the log of the concentration ratio is 1, and t_- refers to a mean concentration of 0·05. Thus, from (*a*), E = 13·6 mv., and from (*b*), E = 14·75 mv.

* Exponent of hydrogen-ion activity; this is essentially pH as usually defined (see Clark, " The Determination of Hydrogen Ions," 3rd edtn., pp. 201, 472).

(c) The experimental potentials over the ranges 0·01—0·001, 0·02—0·002, and 0·10—0·01 were 14—15 mv., agreeing with the values calculated on the assumption that the log of the concentration ratios can be used.

(d) The well-known relation between diffusion potentials and conductivity data will now be applied. In the equation

$$E = 59[(v - 2u)/2(u + v)] \log \gamma_1 C_1/\gamma_2 C_2$$

the velocities v and u will be taken as referring to a mean concentration of 0·05, the corresponding mobilities l_+ and l_- being derived from Kohlrausch's tables at 18°. It has been shown by Noyes and Falk (*loc. cit.*) that the relative values of l_+ and l_- at a given concentration and for a given valency type (still more, of course, for the same salt) do not vary much with temperature between 18° and 25°. Then $l_+ = 57·9$ and $l_- = 46·1$, both at $C = 0·05$. The activities $a_\pm$ or γC refer to $C = 0·10$ and 0·01, and log $\gamma_1 C_1/\gamma_2 C_2 = 0·91$. Therefore $E = 59 \times (-0·335) \times 0·91 = -18·0$. If the activity coefficients of the ions, $\gamma_+ = 0·887$ and $\gamma_- = 0·662$, are multiplied by the mobilities l_0 at 25°, then $t_- = 0·45$, f$(t_-, z) = -0·325$, and since at 25° log $\gamma_1 C_1/\gamma_2 C_2 = 0·92$, $E = 59 \times (-0·325) \times 0·92 = -17·6$.

(e) Activity coefficients are calculated from known ionic strengths, I, *i.e.*, for 0·10, 0·05, and 0·01N-potassium sulphate, by the Debye–Hückel equation :

$$-\log f_\pm = 0·505 z_+ z_- \sqrt{I} \text{ or } -\log f_i = 0·505 z_i^2 \sqrt{I} \text{ at } 25°.$$

The same assumptions are made as in (d), *i.e.*, the individual coefficients of the ions $f_i \times {}_0l$ are used in the transport-number factor equation (4), and the mean activities in the log activity ratios. In the present case, $I = 0·075$, $-\log f_+ = 0·138$, $f_+ = 0·728$, $-\log f_- = 0·502$, $f_- = 0·315$, $-\log {}_2f_\pm = 0·124$, $-\log {}_1f_\pm = 0·390$. Therefore $E = 59 \times (-0·518) \times 0·734 = -22·4$.

It is thus evident that the introduction of activities into either (d) the conductivity equations or (e) the equations based on ionic strength, leads to high values of transport-number factors, which are only partly compensated for by the fact that log ratios of $a_\pm$ are lower than log ratios of C. The net result is that the diffusion potentials calculated are far higher than those observed. At concentrations higher than 0·05 and with the higher-valent complex cyanide ions, these disparities are still more marked. A few results are quoted below. Until, therefore, further mathematical analysis has revealed the causes of these discrepancies, it seems better in comparing results to use limiting mobilities and log concentrations throughout.

The transport numbers of bivalent cations in salts of type BA₂ have been extensively studied by Dole and his collaborators and found to vary considerably with concentration. The presence of an intermediate ion has been postulated in these cases. Bivalent anions have received less attention, but Noyes and Falk (*loc. cit.*) refer to them in these terms : "If the transport number of any tri-ionic salt is found constant through a considerable range of concentrations, it makes it somewhat probable, although it does not prove, that the intermediate ion is not present in considerable proportion in the solution." The present results, then, agree with the idea that the only ions present are K⁺ and SO₄⁻⁻, and that the mobilities l_+ and l_- are either nearly constant or vary in nearly the same proportion, l_- or vF decreasing slightly faster than l_+ or uF. Suppose that the whole of the sulphate is present as an intermediate ion KSO₄⁻; then it can be shown that there must be a certain relation between its velocity v_1 and that of the bivalent ion v_2 in order that f(t_-, z) should be nearly constant for the two kinds of ion or for any mixture. The relation is $v_1 = 3uv_2/(v_2 - 4u)$, *i.e.*, in the present case, $v_1 = 47·5$. This, however, would reduce the transport number t_- from 0·523 to 0·393. Since t and f(t_-, z) are found simultaneously and by independent methods to be nearly constant, it follows that there is only a minor proportion, if any, of an intermediate ion present in solutions up to 0·1N.

Measurements on Potassium Ferricyanide.—The conductivities of solutions of this salt at 25° have been determined by Schoch and Felsing (*J. Amer. Chem. Soc.*, 1916, **38**, 1928), and some values at low concentrations have been added by Hartley and Donaldson (*loc. cit.*), who give the highest value of $\lambda_0 = 174·4$, which, when combined with l_+ for K⁺ = 73·5, gives $l_- = 101$, $t_- = 0·578$, and f$(t_- z,) = 0·23$. The values of t_- were determined by Hartley and Donaldson (*loc. cit.*), using the method of moving boundaries, and when extrapolated to $C = 0$ they are in perfect agreement with those based on limiting conductivities. They can also be calculated by the Onsager equation, the limiting values being used (fourth line) :

C	0·00	0·01	0·05	0·10
t_- (exptl.)	0·578	0·568₅	0·560	0·557₅
f(t_-, z)	0·23	0·24₄	0·25	0·25₆
t_- (Onsager)	(0·578)	0·561₅	0·541	0·525₅
f(t_-, z)	(0·23)	0·25	0·28	0·30
E (exptl., transport numbers)	13·6	14·4	14·8	15·1
E (Onsager)	(13·6)	14·8	16·5	17·7

When the calculated E values are compared with those obtained experimentally (marked * in Table I), they are seen to be in satisfactory agreement. Clearly, the introduction of the log activity ratio a (either from γC or from $f_\pm C$) would make the calculated values far too low. If, on the other hand, the transport-number factor is calculated from the activities assigned by the Debye–Hückel equation, then, on account of the low value of a tervalent ion, the factor soon approaches its limiting value of 1 (*i.e.*, when l_- and $v = 0$). Although the log activity ratio is also low, this does not compensate for the above, and the calculated E is too high, as already found in the case of potassium sulphate. Thus, for potassium ferricyanide at $C = 0·05$, $\sqrt{I} = 0·316$, $-\log f_+ = 0·160$, $f_+ = 0·692$, $-\log f_- = 1·440$, $f_- = 0·0363$; therefore $t_- = 0·067$, and f$(t_-, z) = 0·91$. At $C = 0·10$ and 0·01, respectively, $-\log {}_1f_\pm$ and $-\log {}_2f_\pm$ are 0·679 and 0·214₅, hence log $\gamma_1 C_1/\gamma_2 C_2 = 0·545₅$. Therefore $E = 59 \times (0·91) \times 0·545₅ = 29·3$. A modification of the Debye–Hückel equation has been suggested by Kielland (*J. Amer. Chem. Soc.*, 1937, **59**, 1675), *i.e.*,

$$\log f_i = -0·5 z_i^2 \sqrt{I}/(1 + z_i \sqrt{I}) \text{ (inorganic ions)}$$

and

$$\log f_i = -0·5 z_i^2 \sqrt{I}(1 + 2\sqrt{I}) \text{ (organic ions, including ferricyanide)}$$

Application of this to the same ferricyanide solution gives $-\log f_+ = 0·120$, $f_+ = 0·76$, $-\log f_- = 0·875$, $f_- = 0·1334$, f$(t_-, z) = 0·92₃$, which does not greatly affect the value of E, provided that the log activity ratio remains the same. The use of activity equations in general leads to very low transport numbers of multivalent ions at moderate concentrations, and therefore to high diffusion potentials.

Conductivity data alone may be used to calculate the potentials with the aid of certain assumptions. The best agreement is obtained by assuming that l_+ of the potassium ion is the same as that in potassium chloride at the same normality. Then $l_- = \lambda - l_+$ is found to diminish with increasing concentration although not nearly so fast as the activity equations would indicate. Thus at $C = 0·05$, $\lambda = 121·4$, $l_+ = 65·3$, $l_- = 56·1$, $t_- = 0·46₃$, and f$(t_-, z) = 0·38₃$; at $C = 0·10$, $\lambda = 113·5$, and at $C = 0·01$, $\lambda = 141·7$; hence log $\gamma_1 C_1/\gamma_2 C_2 = 0·90₅$ and $E = 21·0$.

TABLE I.

Solutions I, II	1.0, 0.1	0.4, 0.04	0.2, 0.02	0.1, 0.01	0.1, 0.002	0.1, 0.001
E, obs., mv.	20	20.1	19.0 *	17.2 *	30 (17.7)	35 (17.5)

or if (E) is reduced to log $C_I/C_{II} = 1$,

Solutions I, II	0.05, 0.005	0.02, 0.002	0.02, 0.001	0.01, 0.002	0.01, 0.001
E, mv. (as above)	15.1	15.4 *	19.9 (14.6)	10.5 (15.0)	14.0

A line obtained by plotting E against $(C_I + C_{II})/2$ when $C_I/C_{II} = 10$ leads to $E = 12$—13 mv. at $C = 0$. The corresponding value from the extrapolated λ_0 and also $_0t_-$ is 13.5. At higher concentrations the observed values of E fall between those calculated from λ and those from t_-. From about $C = 0.1$, E is 19—20 mv., and potentials then remain constant up to the highest concentrations investigated. A comparison at $C = 0.10$ shows the extent of agreement between the different methods :

(a) From the experimental transport numbers, $t_- = 0.56$, $f(t_-, z) = 0.255$, $l_- = t_-\lambda = 63.5$ ($\lambda = 113.5$). (b) From the Onsager equation applied between $C = 0.0$ and 0.1, $t_- = 0.53$ and $l_- = 60.5$. (c) From $E = 19.0$ mv., $f(t_-, z) = 0.32$, $t_- = 0.52$ and $l_- = 58$. (d) From the conductivities alone, $t_- = 0.44$, $l_- = 50.0$. (e) At the higher mean concentration of 0.55, $E = 20.0$, $f(t_-, z) = 0.34$, $t_- = 0.495$, $l_- = 0.495 \times 98 = 49$.

In these calculations it is assumed that the only ions present are K^+ and $[Fe(CN)_6]^{3-}$. Although the values in (b) and (c) are in fair agreement, there is a discrepancy between (a) the transport number 0.56, which would require $f(t_-, z) = 0.255$, and (c) the transport-number factor 0.32 from E. On the other hand, $f(t_-, z) = 0.255$ would correspond to $E = 15.0$, which is quite out of the question, since the potentials are very steady at these higher concentrations, and persist unchanged over a large range. The hypothesis of an intermediate ion, sometimes postulated, is attractive from several points of view. The strong interionic attraction of a multivalent ion appears to lead to the immobilisation of the cation in such an ion as $[KFe(CN)_6]^{2-}$. This hypothesis may be tested as follows. The mobility of $\frac{1}{2}[KFe(CN)_6]^{2-}$ may be taken provisionally to be the same as that of $\frac{1}{2}[Fe(CN)_5(NO)]^{2-} = 72.5$ (Burrows and Turner, J., 1919, **115**, 1429). The mobility of $[Fe(CN)_6]^{3-}$ being 101, the fraction x of 1 g.-ion of ferricyanide is found which must be transformed into $1 - x$ of $[KFe(CN)_6]^{2-}$ in order to give the observed transport number $t_- = 0.56$ at $C = 0.10$. A special form of equation (2) is used, viz.,

$$-t_- = [v_3z_3x + v_2z_2(1-x)]/\{v_3z_3x + v_2z_2(1-x) + u[z_2 + (z_3 - z_2)x]\}$$

in which the denominator [see equation (2)] is the sum of the product of the velocity, the concentration, and the valency for each ion. From this, with $v_3 = 101$, $v_2 = 72.5$, and $u = 73.5$, we have $x = 0.65$.

The transport-number factor $f(t_-, z)$ for a salt giving several kinds of anions can be obtained from the equation

$$f(t_-, z) = \frac{1}{z_3} \cdot \frac{v_3z_3x}{D} + \frac{1}{z_2}\frac{v_2z_2(1-x)}{D} - \frac{u[z_2 + (z_3 - z_2)x]}{D}$$

where D is the above common denominator. Applying this to the present case, we have $f(t_-, z) = v_3x/(D) + v_2(1-x)/D - u(2+x)/D = -104/442.7_5 = -0.23_5$. This is lower than any of the values calculated from (a) transport numbers, (b) conductivities, or (c) diffusion potentials, on the assumption that the only anion present is $[Fe(CN)_6]^{3-}$. Also the value of the equivalent conductivity, λ, calculated from the mobilities of the ions (including the intermediate ion) given above would be $442.75/3 = 147.5$, as against the observed 113.5. On the other hand, if x is calculated from $3\lambda = 340.5$, i.e., $\lambda = \Sigma l_- + \Sigma l_+$, then $x = 0.21$. The corresponding value of t_- is 0.52 and the factor is 0.248,* again below any experimental value. In fact, no value which can be assigned to the mobility of the intermediate ion is in agreement simultaneously with the experimental results (a), (b), and (c) above.

Measurements on Potassium Ferrocyanide.—The conductivities of this salt at 25° have been determined by Noyes and Johnston (*J. Amer. Chem. Soc.*, 1909, **31**, 987) and by Schoch and Felsing (*loc. cit.*). The extrapolated value of λ_0 is 185.5; therefore l_0 for $\frac{1}{4}[Fe(CN)_6]^{4-}$ is 112. The ratio of this to l_0 for $\frac{1}{3}[Fe(CN)_6]^{3-}$ is 1.11, instead of 1.33 by the valency rule. The values of λ diminish with concentration more rapidly than those of the ferricyanide. Assuming, as before, that l_+ for K^+ has the value which is found in a solution of potassium chloride having the same concentration, the values of t_- and l_- are found to diminish rapidly, as shown in Table II. In this table the Onsager equation has also been used

TABLE II.

Transport numbers of potassium ferrocyanide from conductivity values.

C, g.-equiv./l.	0.00	0.002	0.005	0.010	0.020	0.050	0.100	0.200	0.500	1.00
λ	185.5	160.1	146.9	135.3$_5$	123.3	108.3	98.2	89.7$_5$	81.0	77.2
a	1.00	0.86$_5$	0.794	0.732	0.667	0.586	0.530	0.485	0.438	0.417
l_	112	87.9	75.9	69.7	55.0	43.0	34.7	28.7$_5$	23.1	20.2
t_	0.603	0.555	0.515	0.485	0.445	0.396	0.353			
f(t_, z)	0.245	0.315	0.355	0.385	0.443	0.503	0.555			
t_ (from Onsager's equation)		0.5470	0.524							
f(t_, z) ,, ,, ,,		0.3160	0.345							

to give a value of t_-. Thus $dt_+/dc = 0.25$, and if $t_- = 0.603$ at $C = 0.0$, then at $C = 0.05$, $\Delta t_- = -0.056_5$ and $t_- = 0.54_6$; t_- derived from the diffusion potential is 0.53. In general, values of t_- derived from E agree well with those from the Onsager equation, even up to concentrations above 0.1, at which this equation would not be expected to apply. Thus at $C \sim 0.1$, t_- (from E) = 0.516 and t_- (from Onsager's equation) = 0.523$_5$; whereas at $C \sim 0.275$, $t_- = 0.447$ in both cases.

By plotting E against $(C_I + C_{II})/2$, a linear graph is obtained, which on extrapolation gives $E = 14.5$ at $C = 0$.

The production of one or more intermediate ions from the ferrocyanide is rendered more probable by the higher ionic charge, and the data were therefore examined by methods somewhat similar to those used with the ferricyanide. In potassium ferrocyanide, the presence of osmotically inactive molecular species is shown by the osmotic (freezing-point) activity coefficient $i = 3.57$, and a high proportion of electrically inactive molecules is shown by the conductivimetrically determined $i = 3.37$; both values of i relate to $C = 0.05$ g.-equiv./l. (Noyes and Johnston, *loc. cit.*). The diminution in activity may, however, also be due to the formation of intermediate ions. If the mobilities of all ions are assumed to be the limiting values $_0l$, then it is clear that *all* the anion must be present as $[KFe(CN)_6]^{3-}$ and $[K_2Fe(CN)_6]^{2-}$. The proportion of tervalent ion x can be calculated which will give the observed value of λ, and then the corresponding trans-

* In these calculations the preceding equation for $f(t_-, z)$ is used, and $D = 340.5$.

TABLE III.

Diffusion potentials of potassium ferrocyanide.

C_I, C_{II}, and mean.	log $(aC_I)/(aC_{II})$.	E_d, calc. from λ.*	E, obs.†	C.	E, calc. by Onsager's equatn.
0·5, 0·05; 0·275	0·87$_4$	31·5	26·0		
0·4, 0·04; 0·22	0·87	31·0	24·3		
0·2, 0·02; 0·11	0·86	28·5	21·5	0·10	20·4
0·1, 0·01; 0·055	0·86$_1$	25·9	20·2	0·05	18·7
0·1, 0·005; 0·0525	1·12$_5$	33·5	26 (20)		
0·1, 0·002; 0·051	1·48$_7$	44·2	32·0 (18·8)		
0·1, 0·001; 0·0505	1·76$_1$	52·2	38·0 (19·0)		
0·05, 0·005; 0·0275	0·86$_8$	23·5	16·0		
0·02, 0·002; 0·011	0·88$_7$	20·6	16·0	0·01	16·4
0·02, 0·001; 0·0105	1·16$_1$	26·6	22·5 (17·3)		
0·01, 0·002; 0·006	0·62$_6$	13·1	10·6 (15·2)		
0·01, 0·001; 0·0055	0·90$_0$	18·1	16·0	0·00	(14·5)

* *I.e.*, f(t_-, z) $\times$ 59 $\times$ log (aC) ratio.
† Values in parentheses are those of E reduced to log $C_I/C_{II} = 1$.

port number can be compared with that calculated from E. Experimental quantities at $C = 0.05$ are : $\lambda = 108.3$, $E = 20$, therefore f(t_-, z) $= -0.34$ and $t_- = 0.53$. From the equation $\lambda = \Sigma l_- + \Sigma l_+$, $x = 0.61$. In this calculation $_0l_-$ of $\frac{1}{4}[KFe(CN)_6]^{3-}$ is taken as 101, that of $\frac{1}{3}[KFe(CN)_6]^{2-}$ as 72·5. The above value of x leads to an activity coefficient $i = 3 + x = 3.61$. This is in agreement with the coefficient determined by cryoscopic methods (above). Now, by the equations already illustrated in the case of potassium ferricyanide, transport numbers and their factors can be calculated which correspond to the intermediate ions. Thus, from $x = 0.61$, $t_- = 0.56$ and f(t_-, z) $= 0.235$. This is far lower than the value corresponding to the diffusion potential at $C = 0.05$. Although mobilities can be assigned to the intermediate ions which would reproduce the experimental transport-number factor, they would then not reproduce the experimental values of $_0\lambda$, t_-, and i. Hence, the theory of intermediate ions fails to overcome the difficulties in interpreting the present results, together with previous data, for potassium ferrocyanide.

Comparison of Potassium Ferri- and Ferro-cyanide.—The limiting values of the quantities expressed by the symbols are in close agreement when calculated (1) from $_0\lambda$ and (2) from E, and can therefore be represented by single sets of figures, which are deduced in the order shown by the arrows in the two cases. Thus, (1) : from $_0\lambda$, by subtracting $_0l_+$, $_0l_-$ is obtained, and hence t_-, and by the use of equation (5) or (6), f(t_-, z) ; also, by the use of (4), E is found. Next, (2) : from E, f(t_-, z) and t_- are obtained, and then $_0l_-$ by the use of $_0\lambda$.

	$_0\lambda$.	$_0l_-$.	$_0t_-$.	f(t_-, z).	E.
	(1) $\longrightarrow$				
K$_4$Fe(CN)$_6$	185·5	112	0·604	0·245	14·5
					$\longleftarrow$ (2)
	(1) $\longrightarrow$				
K$_3$Fe(CN)$_6$	174·4	101	0·578	0·230	13·5
					$\longleftarrow$ (2)

In the solutions approaching limiting dilution, [Fe(CN)$_6$]$^{4-}$ is the more mobile ion, as theory requires, and it is confirmed by diffusion potentials that at low concentrations the ratio of $_0l_4$ to $_0l_3 = 1.11$.

The fact that the potentials of the ferro- and ferri-cyanides only differ by a millivolt at a point obtained by extrapolation suggests that these potentials are equal at $C = 0$. (If Schoch and Felsing's value of $\lambda_0 = 168$ for the ferricyanide is accepted, $t_- = 0.56$, and f(t_-, z) $= 0.25$; *i.e.*, it is practically identical with that of the ferrocyanide.)

If the potentials of the two salts are equal, and log C_I/C_{II} is equal to 1 in each case, then f(t_-, z) is also equal for the ferri- and the ferro-cyanide. If we represent this value by $-a$, then by transposition of equation (6) we have

$$\frac{u}{v_4} + 1 = \frac{1}{_4t_-} = \frac{5}{4}\left(\frac{1}{1-a}\right) \text{ and } \frac{u}{v_3} + 1 = \frac{1}{_3t_-} = \frac{4}{3}\left(\frac{1}{1-a}\right)$$

Therefore, $v_4/v_3 = (4 + 12a)/(3 + 12a)$. If $E = 14.0$ mv., then $a = 0.2375$ and $v_4/v_3 = 1.17$.

The graphs of E against C diverge as C increases, the slopes are very gradual, nearly parallel, and separated by about 3 mv., that of the ferrocyanide being the upper. In the following table, the transport numbers and mobilities of the two ions are compared at $C = 0.05$, 0·10, and 0·20.

The mobilities of ferro- and ferri-cyanide ions at higher concentrations.

	Potassium ferricyanide.			Potassium ferrocyanide.		
C, g.-equiv./l.	0·05	0·10	0·20	0·05	0·10	0·20
t_-(Onsager)	0·541	0·526	0·504	0·546	0·524	0·490
E, mv. (from graph)	17·5	19·0	20·0	19·0	21·5	24·0
f(t_-, z)	−0·297	0·322	0·340	−0·322	0·365	0·407
t_-(from E)	0·525	0·509	0·495	0·542	0·510	0·475

The small but steady differences between the values of E for the two salts at the same concentration, when introduced into equation (6), evidently lead to an approximate equality in t_-, which becomes almost complete at $C = 0.10$, whereas equality is nearly attained from $C = 0.05$ according to Onsager's equation.