[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Fundamental Studies with the Dropping Mercury Electrode. II. The Migration Current[1]

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Introduction

In general, reducible ions reach the surface of the dropping electrode under the influence of two more or less independent forces; a diffusive force, proportional to the concentration gradient between the depleted region at the electrode surface and the body of the solution, and an electrical force, proportional to the electrical potential gradient around the electrode.[3-5] However, when an excess of an indifferent electrolyte is present in the solution the current is carried practically entirely by the indifferent ions, and the electrical force on the reducible ions is nullified. Under these conditions the reducible ions reach the electrode surface only by diffusion, and hence the limiting current is called a diffusion current. The characteristics of the diffusion current have been discussed in detail in a previous paper.[6] In the present paper we shall discuss the characteristics of the limiting current in ion reductions without extraneous electrolyte in the solution, and its quantitative relation to the diffusion current.

Experimentally it is found[7,8] that the initial limiting current in cation reductions without extraneous electrolyte present is roughly twice as large as the diffusion current obtained after an excess of an indifferent electrolyte is added to the solution. The initial limiting current decreases most rapidly with the first small additions of indifferent electrolyte, and finally becomes constant and practically independent of further additions of the indifferent electrolyte when the concentration of the latter has been made about fifty times larger than that of the reducible ions, provided that the excess of electrolyte does not affect the coefficient of diffusion of the electro-reduced ion. This behavior is exemplified by the

TABLE I

INFLUENCE OF VARIOUS CONCENTRATIONS OF POTASSIUM CHLORIDE, POTASSIUM NITRATE, AND HYDROCHLORIC ACID ON THE LIMITING CURRENT OF LEAD CHLORIDE

50 ml. of 0.00095 M PbCl$_2$ plus 0.2 ml. of 0.1% sodium methyl red, with various concentrations of added electrolytes. Temp. = 25°, P = 21.8 cm., $m^{2/3}t^{1/6}$ = 2.28 mg.$^{2/3}$ sec.$^{-1/2}$

Added salt equiv./liter	Limiting current in microamperes		
	KCl	KNO$_3$	HCl
0	17.6	17.6	17.6
0.0001	16.3	16.2	15.7
.0002	14.9	15.0	14.6
.0005	13.3	13.4	12.7
.001	11.8	12.0	11.2
.005	9.8	9.8	9.5
.1	8.35[a]	8.45[a]	[b]
1.0	8.00[a]	8.45[a]	[b]

[a] Corrected for the residual current.   [b] Maxima present, and diffusion currents not well defined.

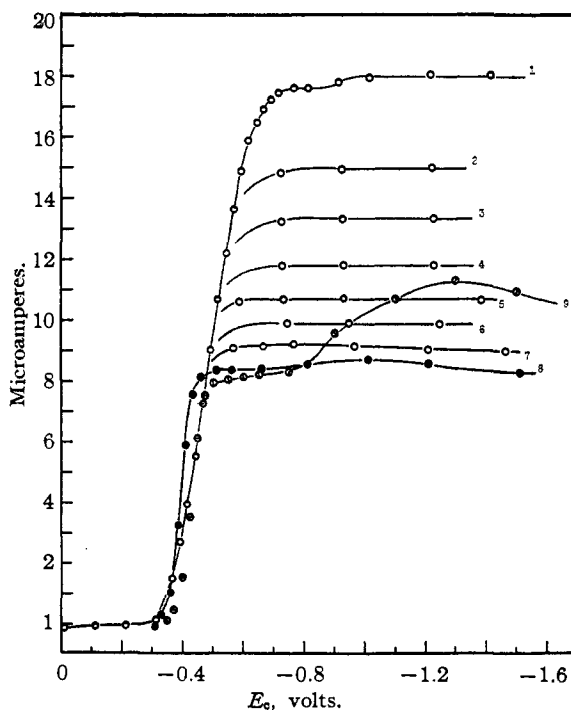typical set of data in Table I, and the current voltage (c. v.) curves in Fig. 1.

Fig. 1.—Influence of various concentrations of potassium chloride on the limiting current of lead ions from lead chloride in the presence of methyl red: 1, no KCl; 2, 0.000198 N; 3, 0.000493 N; 4, 0.00107 N; 5, 0.00179 N; 6, 0.00412 N; 7, 0.0107 N; 8, 0.090 N; 9, 0.90 N.

In the reduction of anions (iodate, e. g.,) it is found that the limiting current without added electrolyte is much *smaller* than the diffusion current obtained in the presence of an excess of indifferent electrolyte (see Table II).

In order to account for these experimental facts, Heyrovsky[9] and Ilkovic[3] assume that the total limiting current, i_1, is in general the algebraic sum of a part i_d due to diffusion, and a part i_m due to electrical migration or transference. In the case of cation reductions the limiting current is increased by the electrical migration, and Heyrovsky and Ilkovic write

$$i_1 = i_d + i_m \text{ (cation reduction)} \quad (1)$$

In the reduction of anions, since the direction of the electric field is such that anions are repelled from the electrode, we have

$$i_1 = i_d - i_m \text{ (anion reduction)} \quad (2)$$

Heyrovsky logically assumes that the migration current, i_m, is equal to the product of the total limiting current and the transference number, T_i, of the reducible cations or anions

$$i_m = i_1 T_i \quad (3)$$

When no extraneous electrolyte is present the transference number will be designated by the superscript (0), i. e., T_i^0, to indicate that it is the transference number in the pure solution of the reducible salt. When indifferent electrolyte is added to the solution the transference number decreases from T_i^0 to some smaller value, T_i, which depends on the relative concentrations of the reducible ions and the added electrolyte, and to a lesser degree on the valencies and mobilities of all the ions concerned. As extraneous salt is added to the solution, T_i decreases and rapidly approaches zero. For example, in a pure 0.001 M solution of lead chloride the transference number of the lead ion is 0.48, whereas if the solution also contains 0.002 M potassium chloride $T_{Pb^{++}}$ is about 0.25, and only 0.05 in a solution 0.02 M in potassium chloride. This accounts for the rapid decrease in the migration current as indifferent electrolyte is added, shown by the data in Table I.

Heyrovsky and Ilkovic[3] assume that the diffusion component, i_d, of the total limiting current is the same in a pure solution of a reducible salt as in a solution containing an excess of indifferent electrolyte. If we represent the initial limiting current with no foreign electrolyte present by i_1^0, and the diffusion current in the presence of an

excess of indifferent electrolyte by i_d, then on the basis of their assumption by combining equations (1) and (2) with eq. 3 we obtain[3]

$$\frac{i_1^0}{i_d} = \left(\frac{1}{1 - T_+^0}\right) \text{ (cation reduction)} \quad (4)$$

and

$$\frac{i_1^0}{i_d} = \left(\frac{1}{1 + T_-^0}\right) \text{ (anion reduction)} \quad (5)$$

However, the assumption of Heyrovsky and Ilkovic that the diffusion component of the limiting current is independent of the presence of foreign electrolyte is not strictly correct. Actually, the diffusion component of the limiting current may change appreciably when foreign electrolyte is added to the solution, due to a change in the effective diffusion coefficient of the reducible ions. According to the Ilkovic equation, the diffusion current is given by[3,5,6]

$$i_d = kD^{1/2} \quad (6)$$

where D is the diffusion coefficient of the reducible substance (cm.^{2} sec.$^{-1}$). When an excess of indifferent electrolyte is present in the solution the effective diffusion coefficient will be the characteristic molar diffusion coefficient of the reducible ions, which at infinite dilution and 25° is given by[5,6,8]

$$D_{ion} = \frac{RT\lambda_i^0}{zF^2} = 2.67 \times 10^{-7} \frac{\lambda_i^0}{z} \text{ (cm.}^2 \text{ sec.}^{-1}) \quad (7)$$

In this equation, which was first derived by Nernst,[10] R is the molar gas constant (8.317 volt-coulombs), T the absolute temperature, λ_i^0 the equivalent conductance of the reducible ions at infinite dilution, z their valence without regard to sign, and F the faraday.[6]

On the other hand, when no foreign electrolyte is present the reducible ions are not free to diffuse independently of the ions of opposite sign, but are constrained to diffuse according to a diffusion coefficient that is intermediate between the characteristic diffusion coefficients of the positive and negative ions of the reducible salt. This diffusion coefficient, which may be designated as D_{salt}, is given by the following equation at infinite dilution

$$D_{salt} = \frac{RT}{F^2}\left(\frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right)\left(\frac{1}{z_+} + \frac{1}{z_-}\right) = \frac{D_+ D_- (z_+ + z_-)}{z_+ D_+ + z_- D_-} \quad (8)$$

In this equation, λ_+^0 and λ_-^0 are, respectively, the equivalent conductances at infinite dilution of the cations and anions of the reducible salt,

(9) J. Heyrovsky, *Arhiv. Hem. i Farm.*, **8**, 11 (1934).

(10) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

and z_a and $\bar{z}_a$ are the corresponding valencies. The derivation of this equation has been discussed in detail by Haskell,[11] Planck,[12] and Lingane.[8]

In a pure solution of a reducible salt the diffusion component of the limiting current, designated by i_d^0, should be given by

$$i_d^0 = kD_{salt}^{1/2} \tag{9}$$

whereas the diffusion current obtained with an excess of indifferent electrolyte in the solution is given by[6]

$$i_d = kD_{ion}^{1/2} \tag{10}$$

Kolthoff and Lingane[5] have shown that the proportionality constant k in these equations (605-$nCm^{2/3}t^{1/6}$) is practically the same without as with indifferent electrolyte present. Since in general D_{ion} will not be equal to D_{salt} (except in the special case when $\lambda_+^0 = \lambda_-^0$ and $z_a = z_a$) it is evident that in general i_d^0 should differ more or less from i_d.

By combining equations 9 and 10 with equations 1, 2, and 3 we obtain the following relations between the initial limiting current without foreign electrolyte and the diffusion current in an excess of indifferent electrolyte

$$\frac{i_1^0}{i_d} = \left(\frac{D_{salt}}{D_{ion}}\right)^{1/2}\left(\frac{1}{1 - T_+^0}\right) \quad \text{(cation reduction)} \tag{11}$$

and

$$\frac{i_1^0}{i_d} = \left(\frac{D_{salt}}{D_{ion}}\right)^{1/2}\left(\frac{1}{1 + T_-^0}\right) \quad \text{(anion reduction)} \tag{12}$$

These equations should be more accurate than the simpler equations 4 and 5.

MacGillavry[4] recently has derived a similar equation for the ratio i_1^0/i_d in cation reduction. In the notation of this paper his equation is

$$\frac{i_1^0}{i_d} = \left(1 + \frac{z_+}{z_-}\right)^{1/2}\left(1 + \frac{z_+\delta_+^0}{z_-\delta_-^0}\right)^{1/2}\left(\frac{\delta_+^0}{\delta_+}\right)^{1/2}\left(\frac{t^0}{t}\right)^{1/6} \tag{13}$$

where δ_+^0 and δ_-^0 are the absolute mobilities (velocity per unit force) at infinite dilution of the cation and anion of the reducible salt, δ_+ is the mobility of the reducible cation in the presence of an excess of added electrolyte, and t^0 and t are the drop times at constant pressure without and with added electrolyte. Since

$$\delta_+^0 = \lambda_+^0/zF^2$$
$$D_{ion} = RT\lambda_i^0/zF^2, \text{ and}$$
$$T_+^0 = \lambda_+^0/(\lambda_+^0 + \lambda_-^0)$$

it can be shown that the *first two* terms in MacGillavry's equation are identical with eq. 11.

(11) Haskell, *Phys. Rev.*, **27**, 145 (1908).

(12) M. Planck, *Wied. Ann.*, **39**, 161, 561 (1890); *Sitzber. preuss. Akad. Wiss.*, 285 (1927); 9 (1929); 367 (1930); 113 (1931).

The third term is a correction for the decrease in the mobility of the reducible cation, and the last term is a correction for the change in drop time, when foreign electrolyte is added to the solution. The change in t when indifferent salt is added is small, unless the added salt is strongly capillary active, and therefore the ratio t^0/t will usually be so close to unity that the last term in eq. 13 safely can be neglected. The essential difference between MacGillavry's equation and eq. 11 is the correction term $(\delta_+^0/\delta_+)^{1/2}$ for the decrease in the mobility of the reducible cation when indifferent electrolyte is added to the solution. However, this difference is more apparent than real, because if experimentally determined values of D_{ion} and D_{salt} are used in equations 11 and 12 these equations are theoretically just as exact as eq. 13.

Experimental data for D_{ion} and D_{salt} are not available for the particular reducible ions and salts with which we are concerned under the conditions of the present experiments. Furthermore, our knowledge of the decrease in the mobilities of individual ions with increasing ionic strength is still too incomplete for exact calculations.[5,6,13] For these reasons, we assumed in the interpretation of experimental data that the various salts and ions behaved as ideal solutes, and calculated the necessary diffusion coefficients by means of equations 7 and 8.

Experimental

In order to test the foregoing relations, we determined the initial limiting currents with no added electrolyte and the diffusion currents in 0.1 or 0.9 N potassium chloride of various thallous salts, lead chloride, cadmium sulfate, and potassium iodate. The various thallous salts (TlCl, TlOH, Tl acetate, and TlIO$_3$) were chosen so that the transference number of the thallous ion would differ as much as possible in the various cases. A trace of sodium methyl red (one or two drops of a 0.1% solution of sodium methyl red per 50 ml.) was added to the solutions to eliminate maxima. Special experiments showed that this very small concentration of sodium methyl red had no appreciable influence on either the initial limiting currents or the diffusion currents.

The apparatus and general technique of the measurements have already been described.[6] The same capillary as in the previous work[6] was used in the present experiments. Air was removed from the solutions with purified nitrogen.

A stock solution of pure thallous hydroxide was prepared in the following manner. A solution of purified thallous sulfate was acidified slightly with sulfuric acid

(13) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

TABLE II

COMPARISON OF INITIAL LIMITING CURRENTS AND DIFFUSION CURRENTS OF VARIOUS REDUCIBLE IONS

Reducible salt	i_1^0 microamp.	i_d microamp.	T_i^e Calcd.	Obsd.	Ratio i_1^0/i_d — Calcd. 1 (Eq. 4)	Calcd. 2 (Eq. 11)
0.001 M TlCl	11.6	6.10[a]	0.500	1.90	2.00	2.00
	11.6	5.95[b]	.500	1.95	2.00	2.00
.0013 M TlOH	13.9	8.15[a]	.277	1.71	1.39	1.66
.0026 M TlOH	26.7	15.85[a]	.277	1.69	1.39	1.66
.0026 M TlC$_2$H$_3$O$_2$	34.2	15.85[a]	.646	2.16	2.83	2.37
.0005 M TlIO$_3$	6.55 (Tl$^+$)	3.30[a]	.646 (Tl$^+$)	1.99	2.83	2.37
.00095 M PbCl$_2$	17.6	8.35[a]	.483	2.11	1.93	2.39
	17.6	8.00[b]	.483	2.20	1.93	2.39
.001 M CdSO$_4$	12.7	8.00[a]	.400	1.59	1.67	1.83
.00015 M KIO$_3$	2.40 (IO$_3^-$)	3.70[a]	.356 (IO$_3^-$)	0.65	0.74[e]	0.84[d]

[a] In 0.1 N KCl corrected for the residual current. [b] In 0.9 N KCl corrected for the residual current. [e] Eq. 5. [d] Eq. 12.

(to prevent the formation of black, insoluble Tl$_2$O$_3$ at the platinum anode) and electrolyzed with a platinum anode and a mercury cathode. The resulting thallium amalgam was washed thoroughly with pure, carbon dioxide-free water, and then was placed in pure, carbon dioxide-free water and decomposed by bubbling a stream of carbon dioxide-free air through it for several hours. The resulting solution of thallous hydroxide was filtered (to remove a small amount of thallic oxide which formed when the amalgam was decomposed), and was standardized by titration with standard acid. Solutions of thallous acetate were prepared by neutralizing portions of the stock thallous hydroxide solution with acetic acid.

The results obtained are given in Table II. The transference numbers of the reducible ions in the pure solutions of the reducible salts, given in the fourth column, were calculated in the usual way by means of the relation $T_+^0 = \lambda_+^0/(\lambda_+^0 + \lambda_-^0)$. The fifth column contains the observed ratios of the initial limiting current to the diffusion current in an excess of potassium chloride. The values of this ratio computed according to the simple equations 4 and 5 of Heyrovsky are tabulated in the sixth column, while the last column contains the values of i_1^0/i_d computed according to eq. 11 or eq. 12.

The values of i_1^0/i_d computed according to equations 11 or 12 are in most cases in better agreement with the observed values of this ratio than the values calculated by means of equations 4 or 5. Cadmium sulfate and potassium iodate are the only exceptions; in these cases equations 4 or 5 gave better results.

The observed values of i_1^0/i_d are in most cases less than the calculated values. This is perhaps due to unavoidable traces of salt impurities in the pure solutions of the reducible salts, which would be sufficient to decrease i_1^0 appreciably, e. g., traces of alkaline impurities from the glass of the cell,

or traces of dissolved mercury from the quiet electrode. In view of the difficulty of completely eliminating such impurities, the agreement between the observed and calculated values of i_1^0/i_d is as good as can reasonably be expected.

It is interesting to note that a correction for the decrease in the absolute mobilities of the reducible metal ions when foreign salt is added, as recommended by MacGillavry,[4] would increase the calculated values of i_1^0/i_d. Hence such a correction actually would increase the differences between the observed and calculated values of this ratio. The data in Table II indicate that such a correction is not justified, and that other unknown factors (specific salt effects, etc.) are operative to a certain degree. The decrease in the diffusion current of lead ions between 0.1 and 1 N potassium chloride (Table I) is an example of such a specific salt effect (probably PbCl$_3^-$ or PbCl$_4^-$ formation).

Increase or "Exaltation" of the Migration Current by the Preceding Discharge of an Uncharged Substance.—Suppose that some uncharged substance, which is reduced more easily (i. e., at a more positive potential) than the reducible ion in question, is added to a pure solution of a reducible salt. The resulting total limiting current (at potentials at which the reducible ions are discharged) will then be the sum of the limiting current of the uncharged substance and that of the reducible ions.[14] That is

$$i_{\text{Total}} = i_u + i_l \tag{14}$$

where i_u is the limiting current of the uncharged substance and i_l is that of the reducible ions. As pointed out by Heyrovsky and Bures,[14] the mi-

(14) J. Heyrovsky and M. Bures, Coll. Czech. Chem. Commun., **8**, 446 (1936).

gration current of the reducible ions under these conditions should be given by

$$i_m = (i_u + i_i) T^0 \qquad (15)$$

and hence should be greater than the migration current without any uncharged reducible substance present. The effect of this "exaltation"[14] of the migration current will be to increase the limiting current in cation reductions, and to decrease it in anion reductions.

If we make the logical assumption that the diffusion current of the reducible ion is unaffected by the preceding discharge of the uncharged substance, it is easily derived[14] that the exaltation in the case of cation reduction should be

$$i_i - i_i^0 = i_m - i_m^0 = i_u \frac{T_i^0}{1 - T_i^0} = i_u \frac{\lambda_+^0}{\lambda_-^0} \qquad (16)$$

where the superscript (^{0}) denotes that no foreign salt was present.

We determined the exaltation of the potassium and sodium ion limiting currents, in solutions of their chlorides, by the previous discharge of oxygen. A set of typical curves is shown in Fig. 2. Curve 1 in this polarogram was obtained with a pure oxygen-free solution of 9.4×10^{-4} N potassium chloride. Curve 2 was obtained after saturating the solution with oxygen.

In curve 2 of Fig. 2 the limiting current of oxygen, i_u, is 28.0 microamp. Since $T_{K^+}^0 = 0.493$ in potassium chloride, we calculate from eq. 16 that the exaltation of the potassium ion limiting current by the preceding discharge of oxygen should be 28.0 (0.493/0.507) = 27.2 microamp. The observed exaltation is 37.0 − 16.2 = 20.9 microamp.

Similar experiments were carried out with 9.4×10^{-4} N sodium chloride. In the absence of oxygen the limiting current of the sodium ions was 12.5 microamp. When the solution was saturated with pure oxygen the limiting current of sodium ions increased to 26.5 microamp., while that of the oxygen was 30.0 microamp. Hence the observed exaltation was 26.5 − 12.5 = 14.0 microamp. Since $T_{Na^+}^0$ in sodium chloride is 0.400, the calculated exaltation is 30.0(0.400/0.600) = 20.0 microamp.

The discrepancy between the observed and calculated exaltation in the foregoing cases is about 25%. The discrepancies can be accounted

for by the fact that hydroxyl ions are a product of the reduction of oxygen, and when the latter is discharging simultaneously with the alkali ions the solution at the surface of the dropping electrode is actually equivalent to a mixture of the alkali chloride and hydroxide. Hence the transference numbers of the alkali ions in the solution at the surface of the dropping electrode are considerably smaller than in the pure solutions of the alkali chlorides, and the exaltation is correspondingly decreased. For example, in the case of potassium chloride, the calculated diffusion current in the absence of oxygen is (1 − 0.493)16.2 = 8.2 microamp. and it was the same when oxygen was discharging. Therefore, the observed migration current when oxygen was discharging was 37.0 − 8.2 = 28.8 microamp. From this value of the migration current, we calculate (eq. 3) that the effective transference number of the potassium ions during the simultaneous discharge of oxygen was 28.8/65.0 = 0.443, instead of the value 0.493 in pure potassium chloride. This corresponds to a ratio of hydroxyl to chloride ions of about $^1/_5$
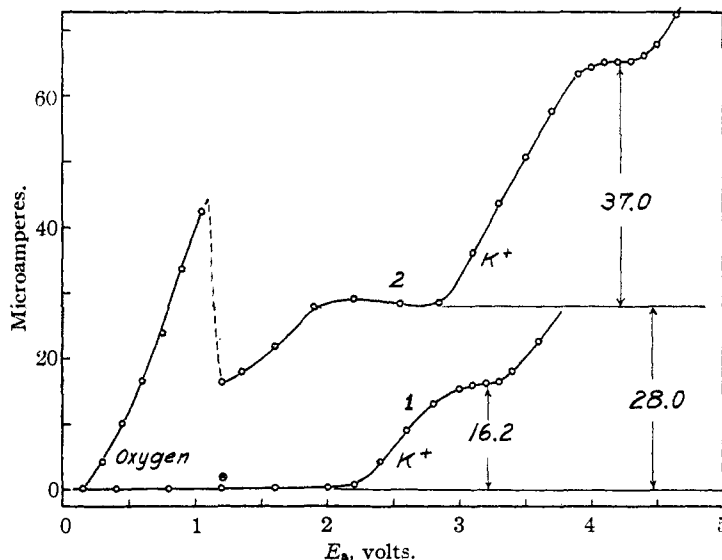

Fig. 2.—Exaltation of the limiting current of potassium ions by the preceding discharge of oxygen.

at the surface of the dropping electrode, which is a logical value.

Heyrovsky and Bures apparently did not recognize the necessity of correcting for this accumulation of hydroxyl ions, probably because they saturated their solutions with air instead of pure oxygen, in which case the correction is much less.

Heyrovsky and Bures state that they also ob-

tained the exaltation effect with barium and manganous ions, and by using other reducible uncharged substances in place of oxygen, e. g., quinone. The reduction of uncharged substances in neutral, unbuffered solutions practically always results in the accumulation of hydroxyl ions at the electrode surface, which must be taken into account.

Exaltation of the Migration Current by the Preceding Discharge of Another Reducible Ion.

—We have found that the migration current (and hence the limiting current) of a reducible cation can be exalted by the preceding discharge of another reducible ion, as well as by the preceding discharge of a non-electrolyte. This effect is shown by the c. v. curves in Fig. 3. Curve 1 in this polarogram was obtained with a pure 9.4×10^{-4} N potassium chloride solution, from which the air had been displaced by purified nitrogen. Curve 2 was obtained after addition of sufficient thallous chloride solution to make the concentration of the latter 8.3×10^{-4} M (the concentration of the potassium chloride being reduced to 8.6×10^{-4} N by the increase in volume).
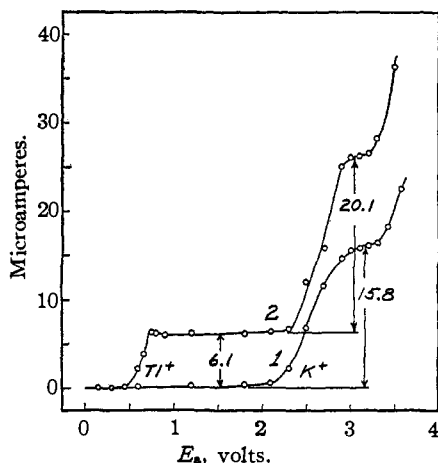

Fig. 3.—Exaltation of the limiting current of potassium ions by the preceding discharge of thallous ions.

Without thallous chloride present the potassium ion limiting current was 15.8 microamp. (curve 1), and it was increased to 20.1 microamp. by the preceding discharge of thallous ions (curve 2). Without thallous chloride present the calculated diffusion current of potassium ions was 15.8 (1 − 0.493) = 8.0 microamp. Since thallous, potassium, and chloride ions all have virtually the same equivalent conductance, the effective diffusion coefficient of the potassium ions was prac-

tically the same with as without thallous chloride present (eq. 7 and eq. 8). However, the diffusion current of the potassium ions was decreased to 8.0 (8.6/9.4) = 7.3 microamp., by the increase in volume when the thallous chloride solution was added. Hence, the migration current with thallous chloride present was 20.1 − 7.3 = 12.8 microamp., whereas the migration current of this same concentration of potassium ions without thallous chloride present was 0.493 × 15.8 (8.6/9.4) = 7.1 microamp.

When the potentials corresponding to the limiting current of potassium ions were reached, in the presence of thallous chloride, the thallous ion migration current, as well as that of the potassium ions, was increased by the increased current. Hence only a part of the apparent increase in the potassium ion limiting current was actually due to the exaltation of the potassium ion migration current, and the remainder was due to the exaltation of the migration current of the thallous ions when they were discharging simultaneously with potassium ions.

In the solution containing practically equal concentrations of thallous chloride and potassium chloride, the transference numbers of the thallous and potassium ions were practically identical and equal to 0.25, while that of the chloride ions was 0.50. Since the total limiting current was 26.2 microamp., the migration currents of the thallous and potassium ions should each have been equal to 0.25 × 26.2 = 6.55 microamp., and the total migration current should have been twice this value or 13.1 microamp. This calculated total migration current agrees very well with the observed value 12.8 microamp.

Although the foregoing exaltation phenomena have little practical value, they do have considerable theoretical significance because they aid in our understanding of the processes in the immediate neighborhood of the dropping electrode.

Summary

1. The equations developed by Heyrovsky, for the relation between the limiting current in ion reductions with no foreign electrolyte present and the diffusion current in the presence of an excess of indifferent electrolyte, have been modified by taking into account the change in the effective diffusion coefficient of the reducible ions caused by the addition of foreign electrolyte.

2. The increase, or "exaltation," of the mi-

gration current of a reducible ion by the preceding discharge of an uncharged substance (e. g., oxygen) has been investigated. Experimental data are given to show that the accumulation of hydroxyl ions at the electrode surface, as a product of the reduction of oxygen, decreases the effective transference number (and hence the exaltation of the migration current) of the reducible ions.

3. It was found that the migration current of a reducible ion can also be increased by the preceding discharge of another reducible ion. The observed exaltation of the migration current of potassium ions by the preceding discharge of thallous ions was in good agreement with the calculated value.

Ionic Character in Diatomic Molecules

BY FREDERICK T. WALL

When one describes the normal state of a diatomic molecule such as a hydrogen halide, it is convenient to refer to it as being partly covalent and partly ionic in character.[1] Qualitatively, from dipole moment values, it is seen that the ionic character of the hydrogen halides decreases with increasing atomic number. However, no simple quantitative way has yet been proposed for estimating the relative contributions of ionic and covalent states to the normal state of a molecule. In this paper there will be shown a method whereby the relative importance of the two states can be estimated quantitatively from a knowledge of the actual potential energy curves and the idealized ionic and covalent curves.

Let us imagine a purely covalent state of a molecule with an electronic wave function ψ_c and also a purely ionic state with a wave function ψ_i. The wave function (unnormalized) for the actual molecule can then be approximated by

$$\psi = \psi_c + a\psi_i$$

where a is a parameter dependent upon the relative importance of the two states. The energy of the system will be given by

$$W = \int \bar\psi H \psi \, d\tau / \int \bar\psi \psi \, d\tau \qquad (1)$$

which upon expansion yields

$$W = \frac{H_{cc} + aH_{ci} + aH_{ic} + a^2 H_{ii}}{1 + 2a\Delta + a^2} \qquad (2)$$

where

$$\Delta = \int \bar\psi_c \psi_i \, d\tau = \int \bar\psi_i \psi_c \, d\tau$$

and

$$H_{ci} = \int \bar\psi_c H \psi_i \, d\tau, \text{ etc.}$$

Each of the quantities a, Δ, H_{cc}, H_{ic}, H_{ci}, H_{ii} and W will be dependent upon the internuclear

separation r. Δ presumably goes to zero as the internuclear separation becomes large.

The actual energy of the molecule will then best be given by minimizing W with respect to the parameter a. Setting $\partial W/\partial a = 0$, there is obtained upon simplification

$$H_{ic} + H_{ci} = \frac{2(a + \Delta)H_{cc} - 2a(1 + a\Delta)H_{ii}}{1 - a^2} \qquad (3)$$

Combining (3) with (2) there is obtained

$$W = (H_{cc} - a^2 H_{ii})/(1 - a^2) \qquad (4)$$

since the term $1 + 2a\Delta + a^2$ cancels out of both numerator and denominator. Solving for a^2 from equation (4) we find

$$a^2 = (H_{cc} - W)/(H_{ii} - W) \qquad (5)$$

Now H_{cc} and H_{ii} are, respectively, the energies which the molecule would have if it were in a purely covalent or a purely ionic state. Although such states are hypothetical, they are nevertheless frequently referred to in speaking of the molecules. Replacing H_{cc} by W_c and H_{ii} by W_i, the equation becomes

$$a^2 = (W_c - W)/(W_i - W) \qquad (6)$$

Empirical Evaluation of a.—From equation (6) it is apparent that a could be determined as a function of r if we knew how W_c, W_i and W depend upon r. Unfortunately curves for W_c and W_i cannot be produced with much certainty. However, an estimate of the value of a at the equilibrium internuclear separation can be made as follows. In accordance with the findings of Pauling and Sherman,[2] assume W_c for a molecule HX to be given by

$$W_c(\mathrm{HX}) = \sqrt{W(\mathrm{H_2})W(\mathrm{X_2})} \qquad (7)$$

(1) Linus Pauling, THIS JOURNAL, **54**, 988 (1932).

(2) Linus Pauling and J. Sherman, THIS JOURNAL, **59**, 1450 (1937).