[CONTRIBUTION NO. 617 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

NEUTRAL SALT ACTION. THE RELATIVE INFLUENCE OF CATIONS AND ANIONS UPON THE EQUILIBRIUM $2Fe(CN)_6^{---} + 3I^- \rightleftarrows 2Fe(CN)_6^{----} + I_3^-$ [1]

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I. Introduction

In a recent paper La Mer and Sandved[2] studied the variation in the stoichiometric equilibrium constant, K_c', corresponding to the reaction

$$2Fe(CN)_6^{---} + 3I^- \leftrightarrows 2Fe(CN)_6^{----} + I_3^-$$

when the system was prepared entirely from potassium salts, with and without addition of potassium chloride. They showed that it was only in the presence of a considerable excess of the foreign neutral salt that constant values for the mass action constant, K'_c could be obtained with varying initial concentrations of potassium ferricyanide and potassium iodide, for any given salt environment.

The purpose of the present paper is to extend these studies to a consideration of the influence of substituting sodium for potassium as cation, and additions of chlorides, nitrates and sulfates in the form of the potassium or sodium salts, to determine whether any marked difference of behavior occurs. Since the reaction involves only ions of negative sign, it seemed reasonable to expect that specific behavior might perhaps be restricted primarily to changes in the nature of the cations and be essentially independent of the nature of the anion, in accordance with Brönsted's theory of specific interaction, even though the concentrations employed exceed the region for which this theory was proposed and verified, namely, at 0.1 N concentrations.[3,4,5]

In view of the renewed interest in the question of the existence of tri-iodides in solution, the data will be considered from two view-points; namely, (a) poly-iodide formation denied, and (b) tri-iodide formation accepted.

II. Experimental Method

The experimental method employed was similar in essentials to that of La Mer and Sandved[6] except that no attempt was made to follow quan-

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[1] Paper presented at the Columbus (April, 1929) Meeting of the American Chemical Society. (Original manuscript received November 10, 1928.)

[2] La Mer and Sandved, THIS JOURNAL, **50**, 2656 (1928).

[3] (a) Brönsted, *ibid.*, **44**, 877 (1922); (b) *ibid.*, **45**, 2898 (1923).

[4] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[5] (a) La Mer and Cook, THIS JOURNAL, **51**, 2622 (1929); (b) La Mer and Goldman, *ibid.*, **51**, 2632 (1929).

[6] Ref. 2, p. 2658.

titatively the rate of attainment of equilibrium. Weighed amounts of the desired salts, potassium ferricyanide, potassium or sodium iodide, and added neutral salt, were dissolved in boiled distilled water in a flask calibrated to contain 100 cc. at 25°. The volume was adjusted to the mark and the flask placed in a thermostat at 25 ± 0.005°, where the mixture was left for three hours to attain equilibrium. That true equilibrium was reached in this time was demonstrated by the fact that no further change occurred in samples allowed to remain in the bath for a longer time.

Six portions of approximately 0.05 *N* sodium thiosulfate solution were weighed out from a weight buret into 500-cc. stoppered Erlenmeyer flasks and diluted to 125 cc. with boiled water. At equilibrium, samples from the reaction flask in the bath were withdrawn with a 10-cc. pipet; 2 cc. of 1% starch solution was added to a portion of the thiosulfate, and then the sample added dropwise from the pipet, which was calibrated in 1/10 cc., permitting readings to 1/100 cc. The sample was added with shaking until a definite color change corresponding to a minute excess of free iodine was produced.

The several factors contributing to the accuracy of this method and its preference over others have been discussed previously. The presence of ferri- and ferrocyanides introduces some difficulty in reading the end-point, since the blue color of starch–iodide appears green in the yellow solution. That this difficulty was overcome by titrating with color standards in a good light is evidenced by the constancy of the ratios of the 6 titers, g. thiosulfate/cc. sample used, whose average value was taken as that for the experiment. The separate ratios, however, generally differed by but several parts per thousand, and the average deviation from the mean considerably less, as shown in the following typical examples.

RATIO, G. $Na_2S_2O_3$/CC. SAMPLE USED

Expt. 9 Poorest agreement accepted	Expt. 18 Average agreement	Expt. 17 Best agreement
(0.2879) (discarded)	(0.3532) (discarded)	0.1110
.2751	.3504	.1112
.2751	.3502	.1118
.2724	.3502	.1118
.2716	.3494	.1110
.2740	.3500	.1112
Av. .2736	Av. .3500	Av. .1113

The titration values for comparable experiments are slightly higher in this than in the previous paper, which we believe to be due to a constant personal error in determining the color standard corresponding to the first permanent appearance of iodine.

The salts used were all of C. P. grade and were twice recrystallized, except the sodium and potassium iodides, which gave no tests for iodine. The thiosulfate solution was restandardized at intervals of two weeks.

Considerable difficulty was encountered in weighing out the sodium iodide, owing to its hygroscopic properties. For that reason the results with sodium salts may not be as accurate as when potassium iodide was used.

III. Data

Table I shows the results of the investigation, the amounts and characters of the added neutral salts being given in Cols. 3 and 4. Column 5 gives the ionic strength, μ, of the systems, and Col. 6 gives x, the *equivalents of titratable iodine* in a liter of the reaction mixture; x is also the moles/liter of the ferrocyanide formed at equilibrium.

It will be noted that when potassium salts are added, the only cation present is the potassium ion, except in Expt. 4. In the case of sodium salts, unfortunately, sodium ferricyanide of sufficient purity was not available at the time, so the potassium ferricyanide was used throughout. The experiments with sodium salts, therefore, contain 0.225 molar potassium ion as cation. This amount of potassium ion is practically insignificant compared to the large amount of sodium ion present, ranging

TABLE I

SHOWING THE INFLUENCE OF ADDED NEUTRAL SALTS ON THE STOICHIOMETRIC EQUILIBRIUM CONSTANT K'_c AND K_c^∞ AT 25°

a = initial concn. of $Fe(CN)_6^{---}$ = 0.075 M $K_3Fe(CN)_6$ (K salt in all cases). b = initial concn. of I^- = 0.20 M KI or NaI as indicated in Col. 2. L_c was taken as 0.00611 (see previous paper)

Expt.	b	Concn. of added salt, m./l.	Added salt	μ	$x \times 10^3$	$C_{I_3^-} \times 10^3$	$K'_c \times 10^3$	$K_c^\infty \times 10^3$
1	K	. . .	. . . . .	0.65	3.356	1.626	0.481	0.0952
2	K	1.0	KCl	1.65	6.743	3.265	4.65	0.881
3	K	2.0	KCl	2.65	9.978	4.831	17.9	3.25
4	K	1.0	NaCl	1.65	5.823	2.822	2.85	0.547
5	K	1.0	$NaNO_3$	1.65	5.497	2.661	2.36	0.454
6	K	0.5	K_2SO_4	2.15	5.954	2.885	3.07	0.588
7	Na	1.0	NaCl	1.65	5.708	2.768	2.67	0.513
8	Na	2.0	NaCl	2.65	8.735	4.228	11.2	2.074
9	Na	3.0	NaCl	3.65	12.27	5.935	37.8	6.656
10	Na	2.0	$NaNO_3$	2.65	7.744	3.751	7.42	1.389
11	K	3.0	KCl	3.65	12.89	6.237	45.4	7.935
12	K	1.0	KNO_3	1.65	6.002	2.908	3.15	0.603
13	K	2.0	KNO_3	2.65	8.115	3.929	8.70	1.622
14	K	3.0	KNO_3	3.65	9.479	4.589	14.9	2.733
15	Na	3.0	$NaNO_3$	3.65	9.578	4.637	15.5	2.830
16	K	3.0	KNO_3	3.65	9.577	4.636	15.5	2.830
17	Na	0.5	Na_2SO_4	2.15	4.976	2.411	1.70	0.330
18	K	4.0	KCl	4.65	15.69	7.585	96.2	16.17
19	Na	4.0	NaCl	4.65	13.84	7.191	64.2	10.22

from 1.2 to 4.2 molar, so that we may for all practical purposes regard the cation as entirely sodium. The influence of interchanging 0.2 *M* of K^+ for 0.2 *M* Na^+ when $\mu = 1.65$ can be seen by comparing the values of K'_c in Table I for Expts. 4 and 7, where the systems are otherwise identical. K'_c is reduced from 2.85 to 2.67, or 6.5%.

IV. The Equilibrium Constants K_c and K'_c

Since the only quantity subject to direct experimental measurement is *x, the number of equivalents of iodine at equilibrium,* we are at liberty to consider this iodine as existing either (a) entirely as molecular iodine or (b) as a mixture of tri-iodide ion and molecular iodine in equilibrium, according to one's preference regarding the question of the existence of tri-iodides. The constants which can be calculated may be derived as follows. Consider the reactions

$$2\mathrm{Fe(CN)_6^{---}} + 2\mathrm{I^-} \leftrightarrows \mathrm{I_2} + 2\mathrm{Fe(CN)_6^{----}} \quad (1)$$

$$\mathrm{I_2} + \mathrm{I^-} \leftrightarrows \mathrm{I_3^-} \quad (2)$$

$$2\mathrm{Fe(CN)_6^{---}} + 3\mathrm{I^-} \leftrightarrows \mathrm{I_3^-} + 2\mathrm{Fe(CN)_6^{----}} \quad (3)$$

where (3) is the sum of (1) and (2). The various concentrations in *moles per liter* may be represented

Initially	At equilibrium
$c_{\mathrm{Fe(CN)_6^{---}}} = a$	$c_{\mathrm{I^-}} = y \quad c_{\mathrm{I_3^-}} = z \quad c_{\mathrm{I_2}} = w$
$c_{\mathrm{I^-}} = b$	$c_{\mathrm{Fe(CN)_6^{---}}} = (a - x)$ and $c_{\mathrm{Fe(CN)_6^{----}}} = x$

since one mole of ferrocyanide is formed for each atom of iodine.

Since in tri-iodide ion only two of the iodine atoms are titratable with thiosulfate, we have

$$x = 2w + 2z \quad (4)$$

Counting the total number of atoms of iodine

$$y + 3z + 2w = b \quad (5)$$

The mass action law for Reaction 2 gives

$$L_c = \frac{c_{\mathrm{I_2}} \times c_{\mathrm{I^-}}}{c_{\mathrm{I_3^-}}} = \frac{wy}{z} \quad (6)$$

Solving (4) and (5) for z and w, we find

$$z = b - x - y$$
$$w = 3/2x + y - b \quad (7)$$

Substituting z and w from (7) and (6) and solving the resulting quadratic in y

$$y = 1/4\ (2b - 2L - 3x \pm \sqrt{(2b - 2L - 3x)^2 + 16L(b - x)}) \quad (8)$$

The mass action law for Reaction 1 gives under assumption (b)

$$K_c = \frac{wx^2}{(a - x)^2y^2} \quad (9)$$

and for Reaction 3 under assumption (b)

$$K'_c = \frac{zx^2}{(a - x)^2y^3} \quad (10)$$

(10) differs from (9) only by the factor L, since

$$\frac{K_c}{K'_c} = \frac{wy}{z} = L$$

when the values for y are taken from (8). The experimental data have been substituted in (10) and the corresponding constants recorded in Col. 8 of Table I. Since the initial c_{I^-} was constant in all of our experiments, it is impossible to determine the relative merits of assumptions (a) or (b). However, when we examine the data of La Mer and Sandved, an extract of which is given in Table II, along with computations for K_c^∞ (see below), we see that although K'_c is an excellent constant for each environment, the corresponding values for K_c^∞ (tri-iodide formation ignored, *i. e.*, L taken as equal to ∞) drift by 33%.

TABLE II

DATA OF LA MER AND SANDVED

Expt.	a = init. $c_{K_3Fe(CN)_6}$	b = init. c_{KI}	Added KCl, m./l.	μ	$K'_c \times 10^3$	$K_c^\infty \times 10^3$
Constant Environment I						
5-6-7 (Av.)	0.075	0.20	1.00	1.65	4.49	0.852
8	.075	.175	1.025	1.65	4.43	.737
9	.075	.15	1.05	1.65	4.45	.641
Constant Environment II						
12	.10	.25	0.825	1.675[a]	4.44	1.03
13	.10	.20	.875	1.675	4.42	0.824
Constant Environment III						
16	.05	.20	1.075	1.575	4.48	.868
17	.05	.15	1.125	1.575	4.51	.662

[a] The μ values (Col. 5) for Expts. 12–15 inclusive of La Mer and Sandved's Table I were erroneously recorded as 1.625 instead of 1.675. The value for K'_c should read 0.199×10^{-1} instead of 0.199×10^{-3}. The last column in Table I should read $10 \times K'_f$ instead of K'_f; *i. e.*, one decimal place was omitted.

Thus the assumption made (but not proved) in the previous paper that one must postulate the existence of tri-iodide ions in order to obtain a mass action constant for a solution of constant environment except for small changes in iodide concentration is fully justified and should assist in removing any doubts which may still persist about the validity of this assumption.[7]

If one desires to find the limiting value of the ratio K_c^∞/K'_c in order to see the relation between these two constants, he may proceed in the following way.

From (6), $z = 0$ when L is set equal to infinity, and from (4) and (5)

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[7] This question was revived with much interest at the Detroit (September, 1927) and Swampscott (September, 1928) meetings of the American Chemical Society, Professor W. D. Bancroft contending that potassium tri-iodide does not exist at 25°.

$w = x/2$ and $y = b\text{-}x$, whence (11) is derivable from (10) by substitution. Call

$$K_c^{\infty} = \frac{x^3}{2(a-x)^2(b-x)^2} \tag{11}$$

as *the constant for Reaction 1* under assumption (a), *i. e.*, K_c^{∞} is the limit of K_c as $L \longrightarrow \infty$. Now let us calculate approximate expressions for y, z, w and K_c^{∞}, under the assumption that L is small in comparison to b, which is true when we set $b = 0.2\ M$ as in the present experiments.

From the identity[8]

$$(2b - 2L - 3x)^2 + 16L(b-x) = (2b + 2L - 3x)^2 + 8Lx$$

we find, extracting the square root to the right by the binomial theorem, and retaining two terms only

$$\sqrt{(2b - 2L - 3x)^2 + 16L(b-x)} = 2b + 2L - 3x + \frac{4Lx}{2b + 2L - 3x} \tag{12}$$

and with the same degree of accuracy, we may replace the expression to the right by $2b + 2L - 3x + (2Lx/b)$. Substituting in (8), we find

$$y \cong b - \frac{3}{2}x + \frac{Lx}{2b} \tag{13}$$

whence by (7)

$$z \cong \frac{1}{2}x - \frac{Lx}{2b} \tag{14}$$

$$w \cong \frac{Lx}{2b}$$

Substituting (13) and (14) in (10), it is seen that

$$K'_c \cong \frac{x^3[1 - (L/b)]}{2(a-x)^2(b - 3/2x)^3} \tag{15}$$

since $Lx/2b$ is negligible in (13).

Dividing (12) by (15)

$$\frac{K_c^{\infty}}{K'_c} \cong \frac{(b - 3/2x)^3}{(1 - L/b)(b-x)^2} \tag{16}$$

or performing the division and retaining only terms of the first degree in L and x

$$\frac{K_c^{\infty}}{K'_c} \cong b + L - \frac{5}{2}x \tag{17}$$

which is of the order of magnitude of b, since L and x are small in comparison to b in these experiments. The reader may verify relation (17) by dividing Col. 9 by Col. 8 in Table I. It will be noted that the ratio is sensibly equal to $b = 0.2$. That is, one may compute K'_c with sufficient accuracy for most purposes directly from K_c^{∞} values using the approximate relation (17) instead of evaluating the quadratic. Equation 17 also shows clearly that the possibility of an error in the determination of L is without appreciable influence upon the values of K'_c in these experiments, since K_c^{∞} is independent of L.

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[8] We are indebted to Dr. T. H. Gronwall for suggesting this development.

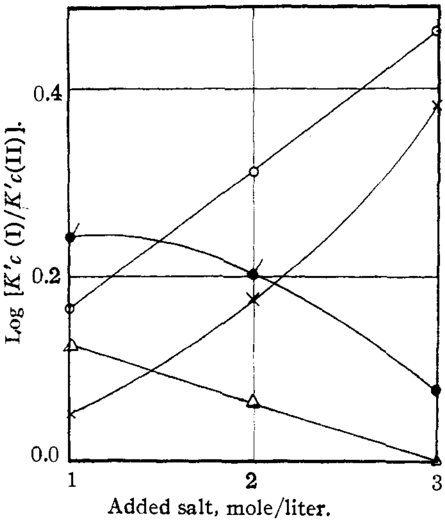
TABLE III

RATIOS OF EQUILIBRIUM CONSTANTS K'_c

Cation (M) present	MX added moles/liter	Ratios expt. no. of Table I	$\frac{K'_c(\mathrm{MCl})}{K'_c(\mathrm{MNO_3})}$	Log Col. 5
K	1.00	2/12	1.476	0.1691
K	2.00	3/13	2.057	.3132
K	3.00	11/16	2.932	.4672
Na	1.00	7/5	1.131	.0535
Na	2.00	8/10	1.513	.1798
Na	3.00	9/15	2.439	.3872
Anion (X) present			$\frac{K'_c(\mathrm{KX})}{K'_c(\mathrm{NaX})}$	
Cl	1.00	2/7	1.742	0.2411
Cl	2.00	3/8	1.594	.2025
Cl	3.00	11/9	1.201	.0795
NO_3	1.00	12/5	1.335	.1255
NO_3	2.00	13/10	1.172	.0689
NO_3	3.00	16/15	1.000	.0000
SO_4	0.50 or 1.00 *N*	6/17	1.806	.2567

V. Discussion

The most striking result of this investigation is the marked specific effect on the equilibrium constants, K'_c or K_c^∞, on changing from potassium to sodium salts and chlorides to nitrates. Thus at 4 molar potassium chloride additions, K'_c = 96.2, while for 4 molar sodium chloride it is 64.2.



○, KCl/KNO_3; ×, $NaCl/NaNO_3$; ●, KCl/NaCl; △, $KNO_3/NaNO_3$.

Fig. 1.

This is best shown in Table III, where we compute the ratios for K'_c (see Col. 4) at constant salt concentrations, when either the cation or anion is changed. The logarithms of these ratios are directly proportional to the change in free energy for Reaction 3 produced by changing the thermodynamic environment. These values are plotted in Fig. 1 against the molality of the added salt. It is to be noted that they are sensibly a linear function of the added salt. The theoretical significance is not entirely clear, but it is interesting to point out that in concentrated solutions the predominant specific term in Hückel's[9] equation for the variation

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[9] Hückel, *Physik. Z.*, **26**, 93–147 (1925).

of the logarithm of the activity coefficient of an ion is linear in respect to concentrations.

If Brönsted's[3] theory of specific interaction were applicable at concentrations higher than 0.1 *M*, we should expect the equilibrium to be practically unaffected by changes in the negative ions and affected only by changes in the positive ions. However, inspection of Fig. 1 shows that the most marked change occurs when Cl is substituted for NO_3, which is not in agreement with this theory.

From the marked change in solubility which iodine exhibits on passing from a nitrate to a chloride solution, it is reasonable to suppose that this failure might be due to the variation in f_{I_2} arising from the formation of complexes of the type I_2Cl^-, as pointed out by Carter.[10]

This hypothesis can be tested by eliminating the variation in f_{I_2} through measurements on the solubility of I_2. We have accordingly computed the values of f_{I_2} in 1, 2 and 3 *M* potassium chloride, potassium nitrate, sodium chloride and sodium nitrate by interpolating the available data on the solubility of iodine in aqueous salt solutions.[11,12,13]

In addition we have determined the solubility of iodine in 3 *M* potassium nitrate and found it to be 0.00083 mole/liter at 25° when the corresponding value in pure water was 0.00134. By subtracting the values of log $[f_{I_2}\text{ (Solvent I)}/f_{I_2}\text{ (Solvent II)}]$ from the corresponding values of log $[K_f(\text{I})/K_f(\text{II})]$ which are equal to log $[K_c^\infty\text{ (II)}/K_c^\infty\text{(I)}]$ where $K_f = \frac{f^2_{IV} \times f_{I_2}}{f^2_{III} \times f^2_{I^-}}$, we should eliminate most of the changes in f_{I_2} due to I_2Cl^- formation or similar mechanisms in passing from Solvent I to Solvent II, *i. e.*, we follow primarily the change in the *ion activity ratio*, $f^2_{IV}/f^2_{III} \times f^2_{I^-}$. According to the principle of specific interaction the values of log $f^2_{IV}/f^2_{III} \times f^2_{I^-}$ should be zero on passing from the chloride to the nitrate solvent but should possess a specific value independent of the anion on passing from potassium to sodium solvents. The result of these calculations shows that the latter conclusion is sensibly correct but the Cl^-/NO_3^- values are not zero although practically independent of concentration. The difficulty may be due in part to the fact that the iodine solubility values of different observers are not consistent. Experiments are now in progress to determine the salt effect on the I_3^- as well as I_2Cl^- equilibria to ascertain whether a better explanation can be obtained by correcting the K'_c values for the variation in $f_{I_3^-}$ and $f_{I_2Cl^-}$, before abandoning the hypothesis of specific interaction as a means of qualitatively predicting equilibria in concentrated solutions in systems of this type.

[10] Carter, *J. Chem. Soc.*, **127**, 2864 (1925); *f* is the stoichiometric activity coefficient.

[11] Herz and Hiebenthal, *Z. anorg. allgem. Chem.*, **177**, 375 (1929), KCl and NaCl.

[12] Carter, Ref. 10, for $NaNO_3$.

[13] McLauchlan, *Z. physik. Chem.*, **44**, 617 (1903), for KNO_3.

It is interesting to note that the experiments of Just[14] on the velocity of the forward reaction between ferricyanide and iodide ion always show a much greater velocity when the system is prepared from potassium instead of sodium salts.

TABLE IV

VELOCITY MEASUREMENTS AT 34.7°

	Init. *a*	Init. *b*	$k_{K^+} \times 10^3$	$k_{Na^+} \times 10^3$	Added salt
1	0.05	0.50	1.56	0.938	....
2	.0125	.50	5.64	3.07	....
3	.05	.375	0.699	0.510	....
4	.025	.50	2.75	1.58	....
5	.025	.50	5.61	...	0.5 *M* KCl
6	.025	.50	4.55	...	0.5 *M* KNO_3

Table IV gives a summary of Just's measurements. k_{K^+} and k_{Na^+} are the velocity constants in the presence of K^+ or Na^+ ions. It will be noted that a greater forward velocity is found for environments in which the equilibrium is displaced most to the right (larger values of K'_c). This holds also for additions of excess of neutral salts like potassium chloride and potassium nitrate.

From the kinetic derivation of the mass law, log K equals log k_1 − log k_2, where k_1 is the velocity constant of the forward and k_2 the velocity constant of the reverse reaction. The evidence at present available indicates that the velocities of reactions between neutral molecules and ions (except for special cases like the action of Cl^- on I_2) are not subject to marked salt effects, whereas reactions between ions are subject to large effects. In the special case where k_2 is independent of the environment, then log k_1 is proportional to log K or to $-\Delta F = RT \ln K$, the driving force of the reaction. The reaction between ferrocyanide and iodine is extremely rapid and thus far we have been unable to measure its velocity satisfactorily to ascertain the influence of salt additions on the reverse reaction.

We wish to thank Professor George Scatchard for constructive criticisms and suggestions in the revision of this paper.

Conclusions

1. The variation in the stoichiometric equilibrium constants K_c and K'_c for the reactions

$$2Fe(CN)_6^{---} + 2I^- \leftrightarrows 2Fe(CN)_6^{----} + I_2 \qquad (K_c)$$
$$2Fe(CN)_6^{---} + 3I^- \leftrightarrows 2Fe(CN)_6^{----} + I_3^- \qquad (K'_c)$$

have been studied in the presence of potassium and sodium ions as cations and also in the presence of additions of nitrates, chlorides and sulfates of potassium and sodium.

2. Marked changes in K_c and K'_c occur on changing from potassium to sodium salts, the constant being larger in the presence of potassium

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[14] Just, *Z. physik. Chem.*, **63**, 538 (1908).

than for sodium salts. The free energy differences of the reaction when potassium is substituted for sodium, or chloride for nitrate, are sensibly linear functions of the concentration of added neutral salt for 1, 2 and 3 molar additions.

3. Although all the ions involved are of negative sign, the shift in equilibrium does not follow the principle of specific interaction at these high concentrations.

4. For solutions of constant thermodynamic environment, K_c^{∞} (tri-iodide formation neglected) is not constant when I^- is varied, whereas K'_c (tri-iodide considered) is constant. This furnishes additional evidence for the existence of tri-iodides in solution.

5. The shift in equilibrium on changing the cation from potassium to sodium is in qualitative agreement with the measurements of the greater velocity of the forward reaction in the presence of potassium ions.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

A STUDY OF THE REACTION BETWEEN HYDROGEN SULFIDE AND SILVER

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In many of the elementary textbooks in inorganic chemistry the reaction between silver and hydrogen sulfide under normal conditions is said to give silver sulfide and hydrogen. Since the electro-potential of silver is greater than that of hydrogen, it seems rather peculiar that silver should so readily replace the hydrogen from this weak acid at ordinary temperatures. A difference in electro-potentials is, however, no criterion that the reaction would not take place, because the order of the electromotive series may be reversed in a great many different ways; but the textbooks indicate that the reaction takes place normally under room conditions.

We find several articles in the literature bearing on this subject and different views are expressed. Inasmuch as there is a difference of opinion in the literature, and many textbooks still hold to the simple replacement reaction, it was thought well to investigate the action of hydrogen sulfide on silver under room conditions, while controlling all variables as far as possible.

Historical Review

One of the earliest of the investigators to inquire into the conditions of the reaction between silver and hydrogen sulfide was J. M. Cabell,[1] who found that silver and hydrogen sulfide dried by phosphorus pentoxide

[1] Cabell, *Chem. News*, 50, 208 (1884).