metrically provided great care is taken in the formation of the phosphate precipitate on the one hand, and on the other that special precautions are taken in the titration of iodine liberated by the arsenate precipitate from potassium iodide or the arsenious acid remaining after all the iodine has been expelled. Detailed procedures have been given which have been found to give results comparable with those by the usual gravimetric procedure.

LAWRENCE, KANS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

# THE APPLICABILITY OF THE FERRO-FERRICYANIDE ELECTRODE TO THE MEASUREMENT OF THE ACTIVITIES OF ELECTROLYTES IN CONCENTRATED SOLUTIONS.

BY G. A. LINHART.

Received February 1, 1917.

The two fundamental concepts Fugacity and Activity which were developed by G. N. Lewis[1] have been applied in numerous cases to the study of dilute electrolytic solutions. Concentrated solutions, however, have been studied very little from this point of view. Potassium chloride was chosen for the present investigation because there are sufficient and reliable data in the literature from which to calculate the activity products of the potassium and chloride ions for a considerable range of concentration.

In a paper by Lewis and Sargent[2] on the Potential of the Ferro-Ferricyanide Electrode, it is shown that in the presence of potassium chloride of definite concentrations, the activities of the potassium ferro-ferricyanides are proportional to their total concentrations. This fact suggested the possible use of the ferro-ferricyanide electrode as one of the reference electrodes in the present experiments, the other being the calomel or the silver chloride electrode. The study of the relation between the potentials of the latter two electrodes in different concentrations of potassium chloride has been one of the secondary purposes of the present investigation; and, it was found that the e. m. f. between the silver chloride and the calomel electrodes, over the range of concentrations given in Table I, remained constant[3] at 0.0456 ± 0.0001 volt. The object of measuring simultaneously the ferro-ferricyanide electrode against the silver chloride or calomel electrode, was to test if there is any irregularity in either electrode as the concentration of the potassium chloride

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[1] Lewis, *Proc. Am. Acad. Art. Sci.*, 43, 259 (1907).

[2] Lewis and Sargent, THIS JOURNAL, 31, 355 (1909).

[3] *i. e.*, constant for any one silver chloride electrode. Differently prepared silver chloride electrodes, however, may differ from one another by as much as 0.001 volt.

approaches saturation. Apparently the change in the concentration of the potassium chloride has little effect on the e. m. f. between the silver chloride and calomel electrodes.

In a cell containing on one side a calomel electrode in a certain concentration of potassium chloride and on the other side, an inert electrode (platinum, gold plated) surrounded by a solution of the same potassium chloride containing minute amounts of potassium ferro- and ferricyanides, the single electrode reactions are

$$Hg + \oplus + Cl^- = HgCl \quad \text{(Solid)}$$

$K_3Fe(CN)_6 + \ominus + K^+ = K_4Fe(CN)_6$, and, since there is no liquid potential, the total cell reaction is the sum of the two, namely,

$$Hg + Cl^- + K_3Fe(CN)_6 + K^+ = K_4Fe(CN)_6 + HgCl \quad \text{(Solid)}.$$

Whence, for the e. m. f., we have

$$E_{\text{obs.}} = E_o - 0.05914 \log \frac{(K_4Fe[CN]_6)}{(K_3Fe[CN]_6)(K^+)(Cl^-)}. \qquad (1)$$

While this assumption that all of the potassium ferro- and ferricyanide present is undissociated proves to be in accordance with the experimental results, it does not account for the fact that potassium ferrocyanide and potassium ferricyanide are fairly good conductors of electricity in water solution. It is very probable that this conductivity is due to intermediate ions, and that, in the presence of a large excess of potassium chloride, the formation of these intermediate ions is largely prevented, due to the fact that all three substances have an ion, $K^+$, in common. Therefore, even the primary dissociation of the potassium ferrocyanide and potassium ferricyanide, which may be represented by the equations,

$$K_4Fe(CN)_6 \rightleftarrows K_3Fe(CN)_6^- \quad K^+$$
$$K_3Fe(CN)_6 \rightleftarrows K_2Fe(CN)_6^- \quad K^+,$$

may be expected to be almost completely repressed when the concentration of the potassium chloride is considerable and in large excess as compared with the concentrations of the other substances. The completeness with which this dissociation is prevented by the potassium chloride, will be discussed later in this article.

## Experimental.

The cells for the calomel electrodes were of the type given in a previous paper;[1] the ferro-ferricyanide electrodes were in similar cells but without the side mercury leads. The separatory funnels in this case were replaced by glass tubes filled with mercury, affording contact with the platinum wire which had previously been welded onto a piece of platinum about one centimeter square, and fused into each glass tube. The platinum

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[1] Linhart, This Journal, 38, 2356 (1916).

electrodes thus prepared were gold-plated, and then dipped into solutions which were to be used in the e. m. f. measurements. At the end of about thirty minutes the cells were rinsed several times with fresh portions from the same stock solution and finally filled and the e. m. f.'s measured against the calomel electrodes. The results are given in Table I. The concentrations of the potassium chloride are expressed in mols per 1000 grams of water. The headings are self-explanatory.

TABLE I.—E. M. F. MEASUREMENTS OF THE FERRO-FERRICYANIDE ELECTRODE AGAINST CALOMEL ELECTRODES AT 25°.

| Expt. | (KCl). | $\frac{\sqrt{(K^+)(Cl^-)}}{(\Sigma KCl)}$.[1] | ($K_3Fe[CN]_6$). | ($K_4Fe[CN]_6$). | Eobs. after | | ΔE. | | $E_0$. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 1 hr. | 12 hrs. | Obs. | Cal. | |
| 1..... | 0.050 | 0.790 | 0.00050 | 0.00050 | 0.0609 | .. | 0.0177 | 0.0178 | |
| 2..... | 0.050 | 0.790 | 0.00025 | 0.00050 | 0.0432 | .. | 0.0355 | 0.0356 | 0.2269 |
| 3..... | 0.050 | 0.790 | 0.00050 | 0.00025 | 0.0787 | .. | 0.0179 | 0.0178 | |
| 4..... | 0.050 | 0.790 | 0.00025 | 0.00025 | 0.0608 | .. | .. | .. | |
| 5..... | 0.100 | 0.740 | 0.00100 | 0.00100 | 0.0870 | 0.0870 | 0.0181 | 0.0178 | |
| 6..... | 0.100 | 0.740 | 0.00100 | 0.00050 | 0.1051 | 0.1051 | 0.0362 | 0.0356 | 0.2209 |
| 7..... | 0.100 | 0.740 | 0.00050 | 0.00100 | 0.0689 | 0.0689 | 0.0178 | 0.0178 | |
| 8..... | 0.100 | 0.740 | 0.00050 | 0.00050 | 0.0867 | 0.0867 | .. | .. | |
| 9..... | 0.500 | 0.620 | 0.00250 | 0.00250 | 0.1586 | 0.1586 | 0.0177 | 0.0178 | |
| 10..... | 0.500 | 0.620 | 0.00125 | 0.00250 | 0.1410 | 0.1409 | 0.0355 | 0.0356 | 0.2187 |
| 11..... | 0.500 | 0.620 | 0.00250 | 0.00125 | 0.1765 | 0.1764 | 0.0180 | 0.0178 | |
| 12..... | 0.500 | 0.620 | 0.00125 | 0.00125 | 0.1584 | 0.1584 | .. | .. | |
| 13..... | 1.031 | 0.590 | 0.00500 | 0.00500 | 0.1931 | 0.1931 | 0.0181 | 0.0178 | |
| 14..... | 1.031 | 0.590 | 0.00250 | 0.00500 | 0.1751 | 0.1750 | 0.0356 | 0.0356 | 0.2184 |
| 15..... | 1.031 | 0.590 | 0.00500 | 0.00250 | 0.2105 | 0.2106 | 0.0181 | 0.0178 | |
| 16..... | 1.031 | 0.590 | 0.00250 | 0.00250 | 0.1924 | 0.1925 | .. | .. | |
| 17..... | 1.572 | 0.578 | 0.00500 | 0.00500 | 0.2139 | 0.2139 | 0.0180 | 0.0178 | |
| 18..... | 1.572 | 0.578 | 0.00250 | 0.00500 | 0.1958 | 0.1959 | 0.0359 | 0.0356 | 0.2187 |
| 19..... | 1.572 | 0.578 | 0.00500 | 0.00250 | 0.2317 | 0.2318 | 0.0182 | 0.0178 | |
| 20..... | 1.572 | 0.578 | 0.00250 | 0.00250 | 0.2135 | 0.2136 | .. | .. | |
| 21..... | 2.007 | 0.576 | 0.00500 | 0.00500 | 0.2267 | 0.2266 | 0.0178 | 0.0178 | |
| 22..... | 2.007 | 0.576 | 00.0250 | 0.00500 | 0.2090 | 0.2088 | 0.0356 | 0.0356 | 0.2192 |
| 23..... | 2.007 | 0.576 | 0.00500 | 0.00250 | 0.2446 | 0.2444 | 0.0180 | 0.0178 | |
| 24..... | 2.007 | 0.576 | 0.00250 | 0.00250 | 0.2266 | 0.2264 | .. | .. | |
| 25..... | 3.320 | 0.598 | 0.01000 | 0.01000 | 0.2545 | 0.2543 | 0.0177 | 0.0178 | |
| 26..... | 3.320 | 0.598 | 0.00500 | 0.01000 | 0.2367 | 0.2366 | 0.0353 | 0.0356 | 0.2190 |
| 27..... | 3.320 | 0.598 | 0.01000 | 0.00500 | 0.2720 | 0.2719 | 0.0180 | 0.0178 | |
| 28..... | 3.320 | 0.598 | 0.00500 | 0.00500 | 0.2541 | 0.2539 | .. | .. | |
| 29..... | 4.284 | 0.615 | 0.01000 | 0.01000 | 0.2689 | 0.2688 | 0.0179 | 0.0178 | |
| 30..... | 4.284 | 0.615 | 0.00500 | 0.01000 | 0.2509 | 0.2509 | 0.0355 | 0.0356 | 0.2188 |
| 31..... | 4.284 | 0.615 | 0.01000 | 0.00500 | 0.2864 | 0.2864 | 0.0180 | 0.0178 | |
| 32..... | 4.284 | 0.615 | 0.00500 | 0.00500 | 0.2686 | 0.2684 | .. | .. | |

[1] See Table II.

## Discussion of Results.

It has already been pointed out that since the concentration of the potassium ion from the potassium ferrocyanide and potassium ferricyanide is very small as compared with that of the potassium chloride, there is practically no liquid potential effect, and we should expect concordant values for $E_0$, calculated by means of Equation 1, provided the activities of the reacting substances are proportional, respectively, to their total concentrations. That this is true for the potassium ferro- and ferricyanides at constant potassium-ion concentration is evident from the values for $\Delta E$ in the eighth column of Table I. It remains only to substitute the correct activity product for potassium and chloride ions in Equation 1 to test, by the concordance of the $E_0$ values, the constancy of the ferro-ferricyanide electrode. These activity products were calculated as follows: The e. m. f. values, obtained by MacInnes and Parker,[1] and by Harned[2], from concentration cells with transference, were divided by 0.495, the transference number, and the E's "without transference" thus obtained were substituted into the equation

$$0.05914 \log \frac{(K^+)(Cl^-)}{(0.00098)^2} = E,$$

assuming that the activity product for KCl at 0.001 $N$ is $(0.00098)$.[2] The square roots of the resulting figures were then divided by the total concentrations of the KCl for convenience of plotting. The values thus obtained were plotted accurately to three significant (see last column in table below) figures against the logs of the concentrations, $\Sigma$(KCl), and the figures given in the third column of Table I, and in the results of Lewis and Sargent, and of Schoch and Felsing, were then read off from the curve.

TABLE II.

| $\Sigma$(KCl). | | $-E_{t'}$. | | $-E$. | $\Sigma$(KCl). | $\frac{\sqrt{(K^+)(Cl^-)}}{\Sigma(KCl)}$. | 25°. |
|---|---|---|---|---|---|---|---|
| 0.001 | 0.01 | 0.05600 | MacInnes | 0.1131 | 0.001 | 0.980 | |
| 0.01 | 0.10 | 0.05400 | & Parker | 0.1091 | 0.01 | 0.886 | |
| 0.1 | 0.16 | 0.01044 | Harned | 0.0211 | 0.10 | 0.741 | |
| 0.1 | 0.20 | 0.01536 | Harned | 0.0310 | 0.16 | 0.689 | |
| 0.1 | 0.22 | 0.01802 | Harned | 0.0364 | 0.20 | 0.677 | |
| 0.1 | 0.30 | 0.02475 | Harned | 0.0500 | 0.22 | 0.684 | |
| 0.1 | 0.34 | 0.02785 | Harned | 0.0563 | 0.30 | 0.653 | |
| 0.1 | 0.50 | 0.03637 | Harned | 0.0733 | 0.34 | 0.652 | |
| 0.1 | 0.70 | 0.04443 | Harned | 0.0897 | 0.50 | 0.617 | |
| 0.1 | 1.00 | 0.05287 | Harned | 0.1068 | 0.70 | 0.606 | |
| 0.1 | 1.30 | 0.05910 | Harned | 0.1194 | 1.00 | 0.592 | |
| 0.1 | 1.90 | 0.06843 | Harned | 0.1382 | 1.30 | 0.582 | |
| 0.1 | 2.50 | 0.07572 | Harned | 0.1530 | 1.90 | 0.574 | |
| 0.1 | 3.10 | 0.08165 | Harned | 0.1650 | 2.50 | 0.582 | |
| .. | .. | ... | .... | .. | 3.10 | 0.593 | |
| .. | .. | ... | .... | .. | sat. | 0.630 | (extrapolated) |

[1] MacInnes & Parker, THIS JOURNAL, 37, 1456 (1915).

[2] Harned, *Ibid.*, 38, 1990 (1916).

The $E_0$'s, obtained by means of Equation 1, are given in the last column. It is evident from the concordance of these $E_0$'s, and of those of Lewis and Sargent, given at the end of this article, that between 0.2 *N* and almost saturation of potassium chloride, the ferro-ferricyanide electrode is perfectly reliable, and can be used as a reference electrode[1] in measuring the activity products of many electrolytes. Thus, we might replace the calomel electrode by mercurous sulfate or mercurous phosphate and obtain the activity products of potassium sulfate or potassium phosphate. Similarly, the positive ions in the ferro- and ferricyanides may be replaced by sodium, magnesium, etc., and thus we obtain the activity products of the corresponding electrolytes. This method will be tried also for measuring the activity products of the hydroxides, by means of the hydrogen electrode.

CALCULATIONS OF $E_0$ VALUES FROM THE MEASUREMENTS OF LEWIS AND SARGENT.

| Expt. | ΣKCl. | $\frac{\sqrt{(K^+)(Cl^-)}}{\Sigma(KCl)}$. | Cc. ($K_4Fe[CN]_6$). | Cc. ($K_3Fe[CN]_6$). | $E_{obs}$. | E.[2] | $E_0$.[3] |
|---|---|---|---|---|---|---|---|
| 1.......... | 0.8 | 0.599 | 0.25 | 0.25 | 0.1855 | 0.1805 | 0.2184 |
| 2.......... | 0.4 | 0.634 | 0.25 | 0.25 | 0.1690 | 0.1485 | |
| 3.......... | 0.4 | 0.634 | 0.25 | 0.75 | 0.1970 | 0.1765 | 0.2190 |
| 4.......... | 0.2 | 0.684 | 0.25 | 0.25 | 0.1538 | 0.1168 | |
| 5.......... | 0.2 | 0.684 | 0.375 | 0.375 | 0.1539 | 0.1169 | |
| 6.......... | 0.2 | 0.684 | 0.500 | 0.500 | 0.1540 | 0.1170 | |
| 7.......... | 0.2 | 0.684 | 0.125 | 0.375 | 0.1820 | 0.1450 | 0.2190 |
| 8.......... | 0.2 | 0.684 | 0.250 | 0.500 | 0.1719 | 0.1349 | |
| 9.......... | 0.2 | 0.684 | 0.250 | 0.750 | 0.1824 | 0.1454 | |
| 10.......... | 0.2 | 0.684 | 0.500 | 0.250 | 0.1362 | 0.0992 | |
| 11.......... | 0.1 | 0.740 | 0.25 | 0.25 | 0.1409 | 0.0879 | |
| 12.......... | 0.1 | 0.740 | 0.25 | 0.75 | 0.1694 | 0.1164 | 0.2217 |
| 13.......... | 0.05 | 0.790 | 0.25 | 0.25 | 0.1293 | 0.0603 | |
| 14.......... | 0.05 | 0.790 | 0.25 | 0.75 | 0.1587 | 0.0897 | 0.2264 |

[1] For the change in the e. m. f. with time, see Lewis and Sargent, THIS JOURNAL, **31**, 356 (1909).

[2] These authors measured the e. m. f.'s of the ferro-ferricyanide electrodes of different concentrations of potassium chloride against the normal calomel electrode. These corrected e. m. f.'s, therefore, are the values which would have been obtained if measured against calomel electrodes of the same concentrations of potassium chloride as those in the ferro-ferricyanide cells, respectively. These corrections were obtained by plotting log 1/0.1, log 1/0.01 and log 1/0.001 against the corresponding e. m. f.'s, 0.530, 0.1070 and 0.1630 (see Table II concerning the activity product of potassium chloride), and reading off the desired values from the resulting curve.

[3] These $E_0$ values, which are in good agreement with those of Table I, for the corresponding concentration of KCl, were calculated on the assumption that the potassium ferrocyanide and ferricyanide were of equimolal concentrations, although in the original article the concentrations given for the ferro- and ferricyanides are 0.408 and 0.542, respectively. This would lower the values for $E_0$ consistently by 0.0074 volt. However, since the numerical values for the concentrations of these substances were of no concern in the investigation cited, it is very likely that the typographical errors *ferro* for *ferri* and *molal* for *normal* were overlooked. We would then have 0.408/3 and 0.542/4 for the concentrations of the ferro- and ferricyanides, or practically equimolal.

It is seen that in Expts. 11 to 14 inclusive, as well as in case of Expts. 1 to 8 inclusive of Table I, the concentrations of the potassium ion of the ferro- and ferricyanides, as well as their difference, can no longer be neglected. Nevertheless, no correction will be applied, since there are no means at the present of measuring the exact concentration of the potassium ion of the ferro- and ferricyanides in the presence of potassium chloride in quite comparable amounts. This effect, thoroughly investigated by Schoch & Felsing,[1] is particularly noticeable in their results, where the concentrations of the potassium ferro- and ferricyanides are quite considerable, and, in several cases, even exceed that of the potassium chloride.

CALCULATIONS OF $E_o$ VALUES FROM THE MEASUREMENTS OF SCHOCH AND FELSING.

| Expt. | (KCl). | $\frac{\sqrt{(K^+)(Cl^-)}}{(KCl)}$. | $(K_4Fe[CN]_6)$. | $(K_3Fe[CN]_6)$. | $E_{obs.}$ | E.[2] | $E_o$. |
|---|---|---|---|---|---|---|---|
| 1..... | 0.005 | 0.971 | 0.00500 | 0.00500 | 0.1247 | 0.0009 | 0.2776 |
| 2..... | 0.010 | 0.886 | 0.00500 | 0.00500 | 0.1252 | 0.0182 | 0.2610 |
| 3..... | 0.010 | 0.886 | 0.01000 | 0.01000 | 0.1335 | 0.0265 | 0.2693 |
| 4..... | 0.025 | 0.834 | 0.00500 | 0.00500 | 0.1300 | 0.0455 | 0.2444 |
| 5..... | 0.025 | 0.834 | 0.01000 | 0.01000 | 0.1368 | 0.0518 | 0.2507 |
| 6..... | 0.050 | 0.790 | 0.00500 | 0.00500 | 0.1390 | 0.0700 | 0.2361 |
| 7..... | 0.050 | 0.790 | 0.01000 | 0.01000 | 0.1430 | 0.0740 | 0.2401 |
| 8..... | 0.100 | 0.740 | 0.00500 | 0.00500 | 0.1498 | 0.0968 | 0.2306 |
| 9..... | 0.100 | 0.740 | 0.01000 | 0.01000 | 0.1515 | 0.0985 | 0.2322 |
| 10..... | 0.200 | 0.684 | 0.00500 | 0.00500 | 0.1597 | 0.1227 | 0.2249 |
| 11..... | 0.200 | 0.684 | 0.02500 | 0.02500 | 0.1658 | 0.1288 | 0.2310 |
| 12..... | 0.250 | 0.666 | 0.01000 | 0.01000 | 0.1673 | 0.1358 | 0.2279 |
| 13..... | 0.300 | 0.653 | 0.00500 | 0.00500 | 0.1671 | 0.1396 | 0.2234 |
| 14..... | 0.400 | 0.634 | 0.00500 | 0.00500 | 0.1722 | 0.1517 | 0.2222 |
| 15..... | 0.400 | 0.634 | 0.01000 | 0.01000 | 0.1725 | 0.1520 | 0.2225 |
| 16..... | 0.400 | 0.634 | 0.02500 | 0.02500 | 0.1760 | 0.1555 | 0.2260 |

## Summary.

(1) From e. m. f. measurements between ferro-ferricyanide and calomel electrodes it is shown that for a given concentration of potassium chloride, the activities of potassium ferro- and ferricyanides are proportional to their total concentrations.

(2) Concordant $E_o$ values are obtained by substituting the experimental results of Table I, and those of Lewis and Sargent, into the equation,

$$E_{obs.} = E_o - 0.05914 \log \frac{(K_4Fe[CN]_6)}{(K_3Fe[CN]_6)(K^+)(Cl^-)}$$

for concentrations of potassium chloride between 0.2 *N* and very near saturation, provided the approximately correct activity product of potassium and chloride ions, as calculated from the e. m. f. data given by MacInnis & Parker and by Harned, are used.

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[1] Schoch and Felsing, THIS JOURNAL, 38, 1937 (1916).

[2] See Footnote 2 to the Table of Results of Lewis and Sargent.

(3) It is pointed out that since these $E_0$'s *are* fairly concordant for a definite range of concentration of electrolyte, the ferro-ferricyanide electrode can be used as a reference electrode for measuring activity products of many electrolytes.

(4) In addition to the measurements of activity products of simple electrolytes which are now in progress, an effort will be made also to measure the activity products of polyvalent electrolytes, with the hope of obtaining some definite knowledge concerning intermediate ions.

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# A NOTE ON THE NUMERICAL RELATION OF ATOMIC WEIGHTS TO ATOMIC NUMBERS.

BY REGINALD GRAHAM DURRANT.

Received October 31, 1916.

W. D. Harkins and E. D. Wilson in their papers[1] have reviewed much recent work on the structure of atoms and have contributed some fresh ideas. Special attention is drawn to the fundamental importance of atomic numbers, and prominence is given to the idea that elements of odd and even atomic numbers form two distinct series. For the lighter elements they give the relation

$$W = 2n + \left\{{}^1/_2 + [(-1)^{n-1} \times {}^1/_2]\right\},$$

where $W$ = atomic weight and $n$ = atomic number. In the summary of the second paper they say:[2]

> "In the case of the heavier elements another term enters so that the more general equation may be given
>
> $$W = 2(n + n') + [{}^1/_2 + {}^1/_2(-1)^{n-1}]."$$

W. D. Harkins and R. E. Hall[3] refer to this latter equation and define $n'$ as zero for the lighter elements. They also state: "The atomic weights are a linear function of the atomic numbers." The varying values of the term $n'$ are not published in any of these papers but are given in the table appended to this note, and are compared to the quotients obtained when each atomic weight is divided by the corresponding atomic number.

The graph of $n'$ values is more regular than the other; it approximates on the whole to four straight lines:

(i) A horizontal line along the zero from helium to chlorine,

(ii) A shorter horizontal—titanium to cobalt—when $n' = 2$,

(iii) A very long line—copper to bismuth—which slopes at an angle whose tangent[4] is almost exactly ${}^1/_3$,

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[1] THIS JOURNAL, 37, 6 (1915).

[2] *Ibid.*, 37, 1395 (1915).

[3] *Ibid.*, 38, 2 (1916).

[4] The tangent of the angle, as given in the graph, is rather larger than ${}^1/_3$, so also