The side reaction which generates hydrogen ion must be the oxidation of a sulfur compound to a valence higher than tetrathionate. From considerations of the *p*H maximum and the kinetics of k_a, it is believed that this reaction has the rate law

$$+\frac{d[H^+]}{dt} = k_6[SO_4^{=}][SO_4 \cdot S_2O_3^{=}]$$

where the ion $SO_4 \cdot S_2O_3^{=}$ is the kinetic intermediate postulated in the mechanism. It is known that the particle $S_2O_3^0$ forms complexes with bases of the Lewis type,[12] therefore we prefer this form to that of the isolated particle $S_2O_3^0$. Assuming that a steady state concentration of this complex is present, the rate law

$$+\frac{d[H^+]}{dt} = k_6 \frac{[P^-]^2[CuT_2^{-3}]}{[T^-]}$$

is obtained. So far, it has not been possible to find a means of testing the rate laws for the side reactions since the concentration of dissolved oxygen is not known.

The stoichiometry of the second side reaction is complex so no attempt will be made here to discuss the many possibilities. It was found that some hydrogen sulfide was formed in the course of the experiments. Small amounts of this material were detected by the insoluble sulfides of zinc, cadmium and silver and by its typical odor. There was no trace of colloidal sulfur in any of our experiments.

The specificity of salt effects is easily explained in the case of the anions, but the marked influence of cations is another matter. It is possible that there are small amounts of catalytic impurities in the salts, but this is hardly a satisfactory postulate since it does not explain why one sodium salt of a mineral acid can replace another without specific effects nor does it explain the inhibition by carbonate and other similar ions. In their work on the acid hydrolysis of the lactones, McDevit and Long[13] demonstrated that the ionic polarizability (or ionic volume) of inert ions has a tremendous influence on the reaction rate. The polarizability increases as one goes from lithium to sodium to potassium. Ammonium ion has a larger polarizability than potassium, but it also has a different electronic structure which could explain the observed discrepancy. A similar discrepancy was found for the relationship between perchlorate ion and the halogenide ions.[13]

A search of the literature showed that this order for specific effects of cations is not new. Seven reactions[14] of varying type have rates whose constants were affected by all or part of the following series:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > H^+$$

It has been found that the "salting-in" of hydrogen peroxide is controlled by the same order in cations.[15]

The large variation in the effect of different univalent positive ions on the rate could be explained if complex ions were formed. Since no data have been found in the literature on complex ions with persulfate or $Cu(S_2O_3)_2^{-3}$, this is merely speculation.

Acknowledgment.—This work was supported in part by funds supplied by the Graduate School of the University of Wisconsin and by the Wisconsin Alumni Research Foundation. The criticisms and suggestions of our colleagues are also gratefully acknowledged.

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[12] (a) O. Foss, *Det Kgl. Norske Vidensk. Sels. Skrifter*, No. 2, 83 (1945); (b) J. O. Edwards, *Chem. Revs.*, in press.

[13] W. F. McDevit and F. A. Long, 118th National Meeting of the American Chemical Society on Sept. 7–8, 1950 at Chicago, Illinois.

[14] (a) M. N. Das and S. R. Palit, *J. Indian Chem. Soc.*, **26**, 322 (1949); **27**, 179 (1950); (b) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932); (c) B. Holmberg, *Z. physik. Chem.*, **97**, 134 (1921); (d) W. J. Howells, *J. Chem. Soc.*, 463 (1939); (e) V. K. La Mer and R. W. Fessenden, THIS JOURNAL, **54**, 2351 (1932); (f) K. Nozaki and R. A. Ogg, Jr., *ibid.*, **64**, 697 (1942); (g) K. J. Pederson, *Trans. Faraday Soc.*, **23**, 316 (1927).

[15] M. H. Gorin, THIS JOURNAL, **57**, 1975 (1935).

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[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Potential of the Electrocapillary Maximum of Mercury. II

BY D. C. GRAHAME, E. M. COFFIN, J. I. CUMMINGS AND M. A. POTH

The potential of the electrocapillary maximum of mercury has been measured for a number of electrolytes in water solution. Seven methods have been used in all, six of them new. Five of the methods have been described in Part I; the other two are described here, together with improvements in one of those described earlier. The results are believed to be accurate to within a few tenths of a millivolt in favorable cases. The thermodynamic and kinetic significance of the results is discussed. The behavior of cesium ion in electrocapillary studies is found to be self-consistent in terms of a simple hypothesis. The "rational" potential of the normal calomel electrode is found to be 0.472 volt.

In a previous paper[1] there were described five methods for the determination of the potential of the electrocapillary maximum of mercury and results obtained by these methods were presented for tenth-normal solutions of potassium and sodium chloride. In the present paper two additional methods are described and results are given for a considerable number of electrolytes.

The importance of the measurements to us arises from the fact that they are necessary for the utilization of differential capacity data. In particular, it is known that at the potential of the electrocapillary maximum (e.c. max.) the surface charge density of electricity on the metallic surface is zero and this fact serves to evaluate the constant of integration needed in the integration of the differential capacity.

In addition the potential of the e.c. max. has another kind of direct thermodynamic significance. It is a measure (through the relation $\Delta F = -n\mathfrak{F}E$)

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[1] D. C. Grahame, R. P. Larsen and M. A. Poth, THIS JOURNAL, **71**, 2978 (1949).

of the free energy of transfer of one mole of the insoluble mercurous salt of the anion in question from the interior of the solid salt to the mercury–solution interface, the mercurous ion going to form a part of the metallic phase and the anion remaining as an adsorbed ion.[2] In this use of the equation $\Delta F = -n\mathfrak{F}E$, E is the potential of the e.c. max. referred to a reference electrode composed of mercury in contact with the insoluble mercurous salt of the anion common to the electrolyte.

Experimental Part

Five methods for the determination of the potential of the e.c. max. were described in Part I.[1] For convenience these will be listed here together with descriptive names. In addition there are listed two new methods to be described below.

Method: I, capillary electrometer and differential capacity; II, arrested flow and differential capacity; III drop time and differential capacity; IV, minimum sum of isotension potentials; V, streaming Hg electrode (Absolute); VI, streaming Hg electrode (Differential); VII, differential capacity only.

Method V.—In this method a stream of mercury is allowed to flow through a jagged glass tip into the well deaerated solution under test and the potential of the streaming electrode is measured relative to a suitable reference electrode just as if one were measuring the potential of a galvanic cell. The pressure applied to the mercury is made variable and is adjusted to that value which gives a maximum potential. Two capillaries streaming into the same solution give the same reading when each is adjusted to its optimum pressure. In the earlier work with this method the results tended to be low by comparison with other methods and this has now been found to be at least partly attributable to traces of insoluble mercurous salts which form very readily whenever the cell is exposed even momentarily to oxygen and mercury at the same time and which are very difficult to remove with even the most vigorous cleaning methods. The remedy was to soak the cell in a fairly strong solution of sodium sulfide after it had been cleaned as thoroughly as possible by conventional means and then to take care that in the assembly of the apparatus mercury was not allowed to come into contact with the interior of the cell until all air had been removed by flushing with nitrogen. It did not prove necessary to remove residual oxygen from the tank nitrogen, although this was often done. It was necessary, however, to be very careful not to admit air accidentally during the transfer of solutions from the reservoirs, particularly since there is great danger of leaving air pockets in the connecting tubes. It was also necessary to avoid lowering the pressure in the cell even slightly below atmospheric (as in withdrawing solutions), since this was sufficient to draw air through the ungreased joints or through the nitrogen vent. These comments apply equally to Method VI to be described below.

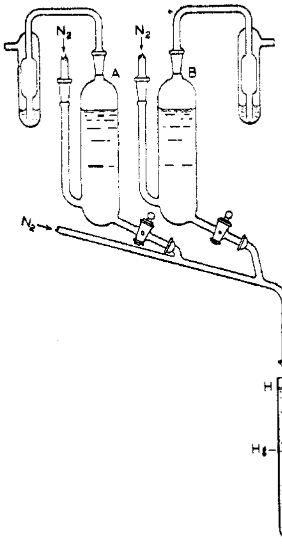

Fig. 1.—Schematic representation of apparatus used to measure potential of the electrocapillary maximum by Methods V and VI.

The apparatus used was essentially like that pictured in Fig. 1 except that only one solution reservoir was needed. (The two reservoirs were needed for Method VI.) It was found to our considerable surprise that the results were unaltered by the use of Apiezon stopcock grease on the joints. This was a great convenience, especially in Method VI, because of the necessity of avoiding the accidental admission of air during the transfer of solutions. Presumably the streaming electrode itself removes capillary-active materials from the solution, which would account for its insensitivity to these contaminants. It was always observed that the potential would start low, rise to a maximum in about half an hour and then descend again. The initial rise we attribute to the cleaning-up process; the final descent we do not understand.

The beneficial effects of using sodium sulfide we attribute to the formation of mercurous sulfide from any remaining insoluble mercury salts in the cell. Mercurous sulfide is so insoluble that the potential of the mercury–mercurous sulfide half-cell lies above the potential of the e.c. max. of the electrolytes studied (with the exception of iodides) so that particles of mercurous sulfide striking the streaming mercury electrode will not be reduced there and will not thereby cause any error. Mercurous chloride and other insoluble mercurous salts, on the other hand, are reduced at a mercury electrode under these conditions and produce a flow of current which unbalances the measuring galvanometer. This probably accounts for the fact that results obtained by this method tend to come out low. The highest value has been regarded as the most reliable in every case, and that is what is reported in the tables under Method V.

Method VI is a modification of Method V. The apparatus used is shown in Fig. 1. Two solutions were stored and deaerated in the reservoirs A and B. It was found that the *difference* between the potentials of the streaming Hg electrode in the two solutions was a good deal more reproducible than either potential alone. This was particularly true when sufficient care was taken to exclude air in the transfer and rinsing processes needed to make the shift from one solution to the other. Since the potential of the e.c. max. was already rather accurately known for tenth-normal potassium chloride[1] and since differences were what we were primarily interested in anyway, a standard value of 0.5589 volt (obtained by Method I) was adopted for the potential of the e.c. max. in that solution measured relative to a tenth-normal calomel electrode.[3]

In using Method VI it is desirable to compare solutions as nearly alike as possible. For this reason the comparison with KCl of a few reference solutions ($BaCl_2$, K_2SO_4, KBr) was made with special care and the remainder of the solutions were then compared each with that solution which it most closely resembled. It was also possible in this way to arrive at a value by two or more paths, thus providing a valuable cross-check on the method.

The use of this method makes the introduction of liquid junctions unavoidable, but as far as solutions of chlorides were concerned, the error could be eliminated completely, at least in principle. What was done was to set up very carefully made silver chloride electrodes in other samples of the solutions under study and to prepare liquid junctions in a manner as nearly as possible identical with that used in Method VI. The potentials of the cells so formed were measured in the usual manner and the results applied as corrections to the measured differences. The only source of error from a thermodynamic standpoint lies in the possible difference in the potentials of the supposedly identical and opposed liquid junctions present in the two experiments. By avoiding as much as possible junctions with large liquid junction potentials, and by taking particular care with those

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(2) D. C. Grahame, *J. Chem. Phys.*, **16**, 1117 (1948).

(3) The value quoted in ref. 1 is 0.5590 volt. That was a rounded-off value of the figure here adopted.

which were unavoidable (particularly the KCl–$BaCl_2$ junction) this error has been held to rather small limits. This method is certainly preferable to one in which each silver chloride or calomel electrode used must be relied upon to be correct at the moment of making the electrocapillary measurements.

The silver chloride electrodes used in the auxiliary experiments just mentioned were made by the method of Noyes and Ellis[4] and were prepared in banks of six to permit accurate intercomparison of supposedly identical electrodes. This was very necessary because some electrolytes (notably rubidium and cesium chlorides) proved difficult to purify to the point where really satisfactory electrodes could be prepared. This fact was revealed by the lack of agreement of the members of a bank, in which case that bank was not employed.

For solutions other than chlorides, liquid junctions were present and their potentials enter into the final tabulated values. This was deliberate, since it gave the information we wanted. The error is not significant, however, since the liquid junction potentials involved were *reproducible* to within the experimental uncertainty, with the possible exception of that between potassium chloride and potassium hydroxide. (Here both the liquid junction potential and the uncertainty of the measurement itself were greater than usual, however, so this is really no exception.)

The values of liquid junction potentials used in the tabulation were computed from the Henderson equation using mobilities at infinite dilution. There is evidence[5] that this is as good a procedure as the more obvious one of using mobilities at the concentration in question and has the further advantage that the necessary data are more certainly known. The uncertainty in the liquid junction potential is rather large, but this is a matter of no real consequence since the data are ordinarily used in a manner such that the assumed value does not enter into the calculations except as a parameter which ultimately drops out. It would be possible, for instance, to assume no liquid junction potential, in which case the results would look a little strange but would contain no thermodynamic inaccuracy.

There is one non-thermodynamic use to be made of the data, however, in which the magnitude of the liquid potential does enter. This is in the estimation of the "rational" potential[6] of the normal calomel electrode, which is a potential difference computed by taking into account only those sources of potential which influence one's measurements, disregarding effects outside the realm of measurement. Because of the uncertainties associated with liquid junction potentials this quantity cannot be determined to an accuracy of better than one or two millivolts.

The materials used for these investigations were purified by recrystallization from conductivity water, except potassium hydroxide and potassium bicarbonate, which were not further purified, and hydrochloric acid, which was purified by distillation in an all-glass apparatus. The number of recrystallizations was generally two.

Method VII is another method (*i.e.*, in addition to Methods I, II and III) which depends upon measurements of the differential capacity. It is quite independent of the other methods involving the differential capacity, however, since it does not depend upon other data and is not influenced in the same way by errors in the data. It depends upon the assumption that at sufficiently large negative polarization the properties of the electrical double layer no longer depend upon the nature of the anion present. This is expected because at these potentials the anions are repelled and can hardly be expected to influence the interface. They do influence the chemical potential of the electrolyte, however, so that the assumption is not altogether unquestionable. The fact that the method works out rather well is perhaps the best evidence of the correctness of the assumption.

What is done in practice is to measure the capacity of the electrical double layer in the manner previously described[7–9] and to assume that at some suitable potential, usually about −1.2 volts relative to a normal calomel electrode, the surface charge density, q, is the same for the electrolyte under test as for another salt of the same cation for which the surface charge density is already known. In the present work, tenth-normal solutions of potassium salts were used and tenth-normal potassium chloride was the electrolyte of known surface charge density. Using the value of q for potassium chloride at −1.2 volts, one integrates the capacity data backwards (toward the e.c. max.) until the potential at which $q = 0$ is found. This is the potential of the electrocapillary maximum. It is a very simple method which works out fairly well in practice. It may be mentioned in passing that the fact that it does work out well speaks for the accuracy of the differential capacity data, upon whose accuracy it is more highly dependent than Methods I, II and III.

Results and Discussion

The results of the investigation are contained in Tables I–III. The accuracy of the results is not everywhere the same. Probable errors have been estimated and indicated by literal superscripts as explained in the legends. These estimates of probable errors are made without regard for the agreement obtained with other methods and have to do only with the self-consistency of the particular method.

TABLE I

POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM AT 25°[a]

Subst.	Concn.	Method	E.c. max. volt	Subst.	Concn.	Method	E.c. max., volt
LiCl	1.0	IV	0.557[d]	HCl	0.1	I	0.557[d]
	0.1	I	.5580[c]			IV	.559[d]
		IV	.559[d]			VI	.558[d]
		VI	.5592[b]	NH_4Cl	.1	I	.5582[c]
NaCl	1.0	IV	.557[d]			IV	.559[d]
	0.1	I	.5585[c]			VI	.5587[b]
		II	.562[d]	$MgCl_2$		I	.5576[c]
		III	.560[d]			IV	.559[d]
		IV	.5585[d]			VI	.5590[b]
		V	.558[d]	$CaCl_2$	.1	I	.5589[c]
		VI	.5591[b]			IV	.559[d]
KCl	1.0	I	.5557[b]			VI	.5586[b]
		II	.555[e]	$SrCl_2$	.1	I	.5582[c]
		IV	.557[d]			IV	.559[d]
		V	.556[d]			VI	.5588[b]
		VI	.5555[b]	$BaCl_2$	.1	I	.5581[c]
	0.7	VI	.5535[b]			IV	.560[d]
	.3	VI	.5515[b]			VI	.5587[b]
	.1	I	.5589[b]	$MnCl_2$	.1	I	.5573[c]
		II	.559[d]			IV	.559[d]
		III	.560[d]			VI	.5589[b]
		IV	.560[d]	$CoCl_2$	.1	I	.5576[c]
		V	.556[d]			IV	.5588[d]
KCl	0.01	II	.600[f]			VI	.5585[b]
		VI	.5936[c]	$NiCl_2$	.1	I	.5573[c]
	.001	V	.640[e]			IV	.558[d]
RbCl	.1	I	.558[d]			VI	.5588[b]
		IV	.5585[d]	$AlCl_3$	.1	I	.5583[c]
		VI	.5576[d]			IV	.559[d]
CsCl	1.0	IV	.556[d]			VI	.5585[b]
	0.1	I	.558[d]	$LaCl_3$	.1	I	.5570[c]
		IV	.559[d]			IV	.558[d]
		VI	.5564[e]			VI	.5588[b]

[a] All potentials in this table measured relative to a calomel electrode in the solution named. [b] Probable error ± 0.2 mv. [c] ±0.5 mv. [d] ±1.0 mv. [e] ±2.0 mv. [f] ±4.0 mv.

Method VI is so much superior to the others that results obtained by it are regarded as final.

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[4] A. A. Noyes and J. H. Ellis, THIS JOURNAL, **39**, 2532 (1917).

[5] "Potentials of Cells with Liquid-Liquid Junctions," by D. C. Grahame and J. I. Cummings, Technical Report No. 5 to the Office of Naval Research, November 22, 1950. Available at the Library of Congress. Requests for reprints may also be directed to the first-named author.

[6] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947). See p. 452.

[7] D. C. Grahame, THIS JOURNAL, **63**, 1207 (1941).

[8] D. C. Grahame, *ibid.*, **68**, 301 (1946).

[9] D. C. Grahame, *ibid.*, **71**, 2975 (1949).

TABLE II

POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM IN CAPILLARY-INACTIVE ELECTROLYTES AT 25°

All potentials in this table measured relative to a normal calomel electrode in potassium chloride. Correction is made for the liquid junction potential of the electrolyte with potassium chloride solution but not for the liquid junction potential between tenth-normal and normal KCl.

Subst.	E.c. max. Method VI	E.c. max. Method VII	L.j. pot. Henderson, mv.
1.0 *N* NaF	0.472[e]		4.1
0.1 *N* NaF	.474[e]		−0.2
.1 *N* KF	.4714[a]	0.4716[c]	4.1
.1 *N* $KHCO_3$	.4728[b]	.4775[c]	6.1
.1 *N* K_2CO_3	.4734[a]	.4734[c]	5.8
.1 *N* K_2SO_4	.4705[a]	.4697[c]	6.1
.1 *N* KOH	.4767[c]	.479[d]	−15.3

[a] Probable error ±0.2 mv. [b] ±0.5 mv. [c] ±1.0 mv. [d] ±2.0 mv. [e] These values obtained by Method V.

TABLE III

POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM IN TENTH-NORMAL SOLUTIONS OF CAPILLARY-ACTIVE ELECTROLYTES AT 25°

Subst.	Method	E.c. max.[d] volt	E.c. max.[e] volt	L.j. pot. Henderson, mv.
$KC_2H_3O_2$	VI	0.4884[a]		6.9
	VII	.4908[c]		
$KClO_4$	VI	.5074[a]		1.5
	VII	.508[c]		
KNO_3	VI	.5166[a]		0.8
	VII	.515[e]		
KCl	I	.5060[a]	0.5060	0.0
KBr	VI	.5741[b]	.499	−0.3
	VII	.576[c]		
KCNS	VI	.626[c]	.630	1.6
	VII	.630[c]		
KI	VI	.732[c]	.477	−0.1
	VII	.737[c]		

[a] Probable error ±0.2 mv. [b] ±0.5 mv. [c] ±1.0 mv. [d] All potentials in this column measured relative to a normal calomel electrode in potassium chloride. Correction is made for the liquid junction potential of the electrolyte with potassium chloride solution but not for the liquid junction potential between tenth-normal and normal KCl. [e] Potentials in this column measured relative to a mercurous salt electrode in the solution named, *e.g.*, Hg, Hg_2Br_2, KBr(c = 0.1) for potassium bromide.

Only in a few cases do the results obtained by other methods fall much outside of their probable errors, which may be taken as evidence that the estimates of probable error are not far from correct. The most serious discrepancies occur with $KHCO_3$ and KI, where the errors in Method VII appear to be three or four times as great as expected. It must be mentioned, however, that no very reliable method of estimating the probable error associated with Method VII is at hand because independent sets of values of the differential capacity for a given electrolyte were not generally available.

Looking at Table I, and looking at the best values (Method VI) for the various tenth-normal solutions, one sees at once a remarkable constancy which could not have been anticipated. Only rubidium and cesium deviate as much as half a millivolt from the median value, 0.5588 volt, and only one other (lithium) deviates even as much as 0.4 mv. The value for hydrochloric acid is set aside as being much less certain than the others. The low value for cesium chloride is very marked, however, and is doubtless related to the fact that the other electrocapillary properties of cesium salts are unusual. For example, Gouy found[10] a lower value for the interfacial tension of mercury in cesium chloride solution than in other chlorides (a result which we have confirmed) and results obtained in this Laboratory[11] show that the differential capacity of cesium chloride solutions is greater than that of any other chloride at the same concentration. Lithium chloride is at the other end of the scale, incidentally, just as in the present results.

These results indicate that the *small effective radius* of the cesium ion at the interface (indicated by the large capacity) allows it to come closer to the interface and thus to annul a part of the potential difference between the inner and outer Helmholtz planes[12] which would otherwise exist as a result of the adsorption of anions from the solution. This lessened potential difference has two effects. It allows more anions to be adsorbed (lowering the interfacial tension) and it lowers the potential of the e.c. max. The experimental results are seen to fit the hypothesis perfectly. It can be predicted that the effect will not be found with cesium fluoride or sulfate or hydroxide or carbonate since there is no adsorption of these anions at the potential of the e.c. max.

The constancy of the potential of the e.c. max. for the remaining solutions of chlorides is in general agreement with the constancy of their differential capacities[11] and reflects an astonishingly constant effective radius at the interface. It is noteworthy that here again the influence of cationic charge is absent, a result which appears with great regularity in these studies and also in those of certain related fields, such as the rate of ferric ion hydrolysis.[13] The great influence of ionic charge in the coagulation of lyophobic colloids is well known and is in striking contrast to the results here presented. This is the more remarkable in that the two effects might have been expected to be dependent upon much the same properties of the active ion.

When referred to a calomel electrode in the same solution the potential of the e.c. max. in potassium chloride reaches a minimum at a concentration of about 0.3 *N*. The same is certainly true for the other chlorides listed. This is easily understood kinetically (the adsorbed anions build up a potential which is greater, the greater the amount of adsorbed anion), but is more difficult to understand thermodynamically. As mentioned above, the potential in question measures the work required to move one mole of calomel from the solid state to a state on the interface where the mercurous ion lies within the metallic phase and the anion remains at the interface. The *decrease* in the potential as the solution becomes more concentrated is associated with the increasing concentration of adsorbed anions, which makes the surface more

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[10] G. Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

[11] D. C. Grahame, *J. Electrochem. Soc.*, **98**, 343 (1951).

[12] See ref. 6, p. 467.

[13] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 348, 1322 (1949).

TABLE IV

ENTROPY AND ENTHALPY OF TRANSFER OF CALOMEL AT POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM IN KCl AT 25°

dE^s/dT is temperature coefficient of e.c. max. measured relative to a calomel electrode held at constant temperature. A negative value indicates that the potential of the calomel electrode becomes smaller as the temperature of the polarized electrode increases. dE^t/dT is the temperature coefficient of two identical calomel cells in the electrolyte named when the temperature of one is changed. A positive value indicates that the warmer cell is positive to the cooler. dE^g/dT is the temperature coefficient of the e.c. max. measured relative to a calomel electrode in the same electrolyte at the same temperature.

Concn. N	dE^s/dT, mv./deg.	dE^t/dT, mv./deg.	dE^g/dT, mv./deg.	ΔS, e.u. per. equiv.	$T\Delta S$, kcal. per. equiv.	ΔF, kcal. per. equiv.	ΔH, kcal. per. equiv.
1.0	-0.66_0	0.59^a	-0.07	-1.6	-0.481	-12.813	-13.294
0.1	$-\ .58_6$	$.77^b$	$+\ .18_4$	4.2	1.265	-12.892	-11.627

[a] Data of T. W. Richards (*Z. physik. Chem.*, 24, 39 (1897)) corrected to 25°. [b] Data of T. W. Richards (*ibid.*) confirmed by measurements made in this Laboratory.

crowded and produces an unfavorable entropy term, one which tends to disfavor the transfer. The entry of the mercurous ion into the interface is highly exothermic, however, since the over-all process is highly favored from the standpoint of free energy change. This is shown definitely in Table IV where the contributions of ΔH and ΔS to ΔF have been evaluated from the temperature coefficient of the potential of the e.c. max. The process of allowing the mercurous ion to enter the metallic phase is equivalent to the insertion of a medium of almost infinite dielectric constant (the metal) between the charged ions composing the salt molecule. This is clearly a highly exothermic process. As the metallic surface becomes more extensively covered with ions (from a more concentrated solution) the process becomes *more highly* exothermic, however, as is shown by Table IV. The reason for this cannot yet be given.

Capillary Inactive Anions.—Certain anions, notably fluoride, carbonate, hydroxide and sulfate, do not depress the interfacial tension of mercury at the potential of the e.c. max.[10,14] This means[15] that they are not adsorbed on the mercury surface at that potential. The bicarbonate ion is also probably unadsorbed, although the evidence is less complete.

It is expected that the potential of the e.c. max. in these solutions will be the same for all and independent of the concentration, at least so long as the concentration remains low enough so that the activity of the water remains constant. This expectation is reasonably well borne out by the facts, as is indicated in Table II. The high value for potassium hydroxide is most readily explained as being due to the use of too large a value for the potential of the liquid junction between potassium chloride and potassium hydroxide. The value used, −15.3 mv., would have to be lowered to about −11.5 mv. to bring about agreement. The non-thermodynamic character of liquid junction potentials makes it impossible to discuss these matters with more precision.

The median of the values in Table II is 0.4728 volt. The potential between normal and tenth-normal potassium chloride (for which no correction has been made heretofore) amounts to about 0.8 mv. With this correction the "rational" potential of the normal calomel electrode amounts to about 0.472_0 volt. The corresponding value for the tenth-normal calomel electrode is 0.525_7 volt. These values are considerably lower than previous estimates based upon less accurate data.

Capillary-active Electrolytes.—In Table III there are listed results obtained for a number of capillary-active electrolytes, including in this list such ions as the acetate which are only very slightly capillary-active. It is interesting to note that the values referred to a mercurous salt electrode in its own electrolyte do not show any correlation with the solubility of the mercurous salt. It is evident that two conflicting influences are at work, the one tending to make the transfer of the solid salt into the interface easier, the other harder. The strong binding of the ions of mercurous iodide in the lattice of the solid salt, for example, undoubtedly makes the salt transfer harder; the greater concentration of iodide ions already at the interface presumably makes it easier for the same (but unexplained) reason already mentioned in connection with the effect of concentration upon the e.c. max. of potassium chloride.

Summary of Values.—Mention should be made of a summary of values of the e.c. max. prepared by the authors and available elsewhere.[16] This summary contains the results of other investigators calculated to a common reference electrode and interpolated to even values of concentration where necessary. The present results disagree with those of previous investigators by an average of 11 mv.

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(14) D. C. Grahame, *Rec. Chem. Prog.*, 11, 93 (1950).

(15) See ref. 6, eq. 21.

(16) "Thermodynamic Properties of the Electrical Double Layer: Potential of the Electrocapillary Maximum in Aqueous Solution at 25°C.," by D. C. Grahame, E. M. Coffin and J. I. Cummings, Technical Report No. 2 to the Office of Naval Research, August 11, 1950. Available at the Library of Congress. Requests for reprints may also be directed to the first-named author.