It has been shown that the values of "Trouton's constant" increase quite regularly and according to the equation

$$\frac{\lambda'}{T_0} = 17 + 0.011T.$$

The divergences in the case of the associated liquids have been considered to be a measure of the association.

In connection with this paper and the preceding one, I wish to express my very sincere appreciation to Prof. W. Nernst for continued counsel and advice.

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THE FREE ENERGY OF SOME HALOGEN AND OXYGEN COMPOUNDS COMPUTED FROM THE RESULTS OF POTENTIAL MEASUREMENTS.

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I. INTRODUCTION.

ONE of the most important chemical problems of the present time is the determination of the free energy of formation of compounds from their constituents, for it is this quantity and not the heat evolved that is the true measure of chemical affinity. No reaction can take place of itself that is not capable of doing external work, and the maximum amount of such work which a reaction can produce at any constant temperature is called the free-energy decrease of the reacting system. Although this is a vastly more important quantity than the heat evolved by the reaction, it is one which is known in few cases, compared with those for which the heat-effect has been measured. This is partly due to the greater difficulty of determining the value of the free-energy change, and partly to the fact that its importance has not until recently been generally appreciated. Just as in thermochemical investigations, so here the most fundamental data are the (free)-energy changes attending the formation of various chemical compounds out of their elements; for from these data the free-energy change attending any reaction can be calculated by direct summation.

One method of measuring the free-energy change of a chemical reaction is to determine the conditions of its equilibrium. For a reaction of the general type $aA + bB \ldots = eE + fF \ldots$ the work W producible by the conversion of a mols of A and b mols of B at concentrations $C_A{}'$, $C_B{}'$ respectively into e mols of E and f mols of F at concentrations $C_E{}'$, $C_F{}'$ respectively, or the free-energy decrease $-\Delta F$ attending it, is given by the equation:

$$W = -\Delta F = RT\left[\log_e K - \log_e \frac{C'^{e}_{E} C'^{f}_{F} \ldots\ldots}{C'^{a}_{A} C'^{b}_{B} \ldots\ldots} + (e + f \ldots - a - b \ldots)\right]$$

in which K is the equilibrium-constant defined by the equation $\mathrm{K} = \frac{C^{e}_{E} C^{f}_{F} \ldots}{C^{a}_{A} C^{b}_{B} \ldots}$ where C_A, C_B, ……C_E, C_F are any concentrations at which equilibrium prevails. In numerous cases, however, it is impossible to determine the equilibrium constant and therefore it is fortunate that another method is applicable to many reactions—one based on electrical potential measurements.

If the saturated solution of a salt in contact with the salt in the solid phase be electrolyzed at constant temperature between electrodes consisting of the products of decomposition, and if the process be reversible, the work done is that necessary to decompose the solid salt.[1] Conversely, the energy obtainable from this combination when working reversibly as a voltaic cell is the free energy of formation of the solid compound from its constituents. What the solvent is makes no difference in either case, provided it is not decomposed by the electrodes themselves. The solvent might be pure water, or a solution of some other salt in water, or any other liquid, so long as it is saturated with the salt in question. To take a concrete example, the free-energy change attending the formation of silver chloride could be determined either by measuring the decomposition potential between platinum electrodes of a saturated solution of silver chloride in water, or by measuring the potential of the cell: Ag | saturated solution of AgCl | Cl_2. If the cell is reversible, the two results should be identical. The latter is much the more accurate of the two methods, on account of the arbitrariness that generally accompanies the determination of decomposition points.

The free-energy decrease in any such case attending the formation of one formula weight of the solid salt out of its elements is simply the product $\nu \mathrm{EF}$, where ν is the number of equivalent weights in one formula weight, E is the electromotive force of the combination and F the quantity of electricity whose passage

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[1] Bodländer: Z. physik. Chem. 27, 55 (1898).

by Faraday's Law always attends a reaction involving one equivalent. If E is expressed in volts and F in coulombs the free energy will of course be in joules. The negative value of this product may be called simply the free energy F of the salt, that of the elements being taken as zero; and we may write therefore: $F = -\nu EF$. In case, however, one or more of the elementary substances or the compound is gaseous and ΔN mols of the gas are produced in the formation of one formula weight of the substance the free-energy equation becomes: $F = -(\nu EF + \Delta NRT)$.

The electromotive force of the above-mentioned type of cell is, however, made up of the electromotive forces at the two electrodes. Now, in many cases these separate values involved have been measured against some standard electrode for one purpose or another, and are found scattered through the literature. It is the aim of this article to summarize these results; to unite them, making a suitable correction for the potential-difference of the liquid-liquid couple, so as to give the electromotive force of a cell composed of the elementary electrodes and a saturated solution of the salt in question; and to calculate therefrom, as just described, the free energy of the salt itself.

The available data relate mainly to difficultly soluble salts; for the potential-differences of *saturated* solutions against electrodes have as a rule been measured only in the case of such salts. The necessary data also exist for a few gaseous or volatile hydrogen compounds (hydrochloric and hydrobromic acids, water, and ammonia); and computations have therefore also been made for these substances.

2. PLAN OF COMPUTATION AND PRESENTATION OF THE RESULTS.

Throughout this article the combination of an electrode with a solution will be designated a (metal-liquid) couple; the combination of two such couples a (voltaic) cell.

In evaluating the potential-differences of separate couples, the normal "calomel electrode" has always been assumed to have the value —560 millivolts at room temperature.[1] The value assigned to this has no effect, however, upon the final

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[1] Ostwald: Lehrb. allgemeinen Chem., 2te Aufl. 2, 1, 944. At 25° the value is —564 millivolts. See Ostwald-Luther: Physiko-Chemische Messungen, p. 383.

results of this article, for it is eliminated in computing the electromotive force of the kind of cell in question.

No attempt has been made to reduce measurements to uniform temperature, for the necessary data are lacking, the temperature itself sometimes not being stated. As all the measurements have probably been (even in cases where the temperature is not given) made between 15° and 25°, no important error will be made in assuming that the final results apply at a temperature of 18°. The results of different observers vary much more among themselves than the error which might be involved in this assumption.

When the electromotive force is directed from the electrode to the solution, it will be considered positive; in the opposite case, negative. The electromotive force of any cell in the direction through it from left to right as it is written will therefore be the algebraic difference obtained by subtracting from the potential-difference of the first, that of the second couple. These will always be expressed in millivolts, unless otherwise stated.

In the calculation of the free energy it is assumed that one faraday F is equal to 96,600 coulombs[1] and that one joule is equal to 4.184 calories at 18°.[2] The value of the gas-constant R is taken as 8.31 joules per degree or 1.986 calories per degree.[3]

The method of working up the data may best be explained with the help of a concrete example. Let us consider the computation of the free energy of silver chloride. A table was made of the values of all the couples of the type Ag/solid AgCl + solvent, that could be found. They were of course measured against some other couple whose value is known. Very often this other couple was the "normal electrode," but not always. Then the values of all the chlorine couples were tabulated. These were of the type $Pt + Cl_2/Cl_2$ + solvent, with the gaseous chlorine at atmospheric pressure. The couples which had the same solvent were then paired by taking the algebraic difference of their separate potentials, and the electromotive forces of the

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[1] The recent work of Richards and Heimrod (Proc. Am. Acad. 37, 415 (1902)) has led to the value 96,580, and that of Guthe (Bull. Bureau of Standards, 1, 362 (1905)) to 96,560, which are practically identical with the round value given above.

[2] Noyes: Gen. Prin. Phys. Sci., p. 75 (1902).

[3] Ibid. p. 96.

cells of the type $Ag/AgCl+$solvent/solvent$+Cl_2/Pt+Cl_2$ obtained. In case the same couple had been measured by different observers, the values were first averaged before combining with that for the opposite couple.

The best method of presenting the results seems to be to tabulate first only those couples which had to be used in computing the free energy of more than one compound. These are the couples composed of various solutions and of the halogens or hydrogen or oxygen as the electrode. The other couples are used only once, and will be given where they are needed.

In gathering these data the author of this paper has consulted the following files of periodicals: *Jrb. Elektrochem.* Vols. 1-10, 1894-1903 (theoretical part of each volume examined page by page); *Z. Elektrochem.*, Vols. 1-10, 1894-1904; *Z. physik. Chem.*, Vols. 1-52, 1887-1905; *Wied. Beiblätter*, Vols. 8-28, 1884-1904; *Z. anorg. Chem.*, Vols. 1-10, 1892-1895; *J. Physic. Chem.*, Vols. 1-9, 1896-1905. In all these files except the first the indexes or the titles of all the separate articles were examined.

Table I contains the sources from which the data used in the subsequent calculations were obtained. The page numbers refer to the beginning of the article in each case. For the sake of brevity, when a reference is cited subsequently, it will be by the name of the author, and the exact page or table in which the data referred to are found will be added.

TABLE I.—LITERATURE ON THE ELECTROMOTIVE FORCE OF COUPLES CONSISTING OF ELEMENTARY ELECTRODES AND SATURATED SOLUTIONS.

Author.	Reference.
Abegg and Cox,	Z. physik. Chem. 46, 1 (1903).
Behrend,	Ibid. 11, 466 (1893); 15, 498 (1894).
Bodländer and Storbeck,	Z. anorg. Chem. 31, 1, 458 (1902).
Boericke,	Z. Elektrochem. 11, 57 (1905).
Brönsted,	Z. physik. Chem. 50, 481 (1904).
Calame,	Ibid. 27, 401 (1898).
Carveth,	J. Physic. Chem. 2, 298 (1898).
Danneel,	Z. physik. Chem. 33, 415 (1900).
Dolezalek,	Ibid. 26, 321 (1898).
Findlay,	Ibid. 30, 628 (1899).
Goodwin,	Ibid. 13, 577 (1894).
Immerwahr,	Z. Elektrochem. 7, 477 (1900).
Küster and Crotogino,	Z. anorg. Chem. 23, 87 (1900).
Küster and Thiel,	Ibid. 23, 25 (1900).
Lovén,	Z. physik. Chem. 20, 456 (1896).
Luther,	Ibid. 30, 628 (1899); 36, 385 (1901).

Author.	Reference.
Luther and Wilson,	Ibid. 34, 488 (1900).
McIntosh,	J. Physic. Chem. 27, 417 (1898).
Müller,	Z. physik. Chem. 40, 158 (1902).
Neumann,	Ibid. 14, 193 (1894).
Rothmund,	Ibid. 31, 69 (1899).
Sammet,	Ibid. 53, 641 (1905).
Sauer,	Ibid. 47, 146 (1904).
Smale,	Ibid. 14, 577 (1894); 16, 562 (1895).
Thiel,	Z. anorg. Chem. 24, 1 (1900).
Wilsmore,	Z. physik. Chem. 35, 291 (1900).
Zengelis,	Ibid. 12, 298 (1893).

3. LIQUID-LIQUID COUPLES INVOLVED IN SUBSEQUENT COMPUTATIONS.

The electromotive forces of the liquid-liquid couples that are involved in the subsequent computations may next be tabulated. Some of these have been computed by me for a temperature of 17° by the formula derived by Planck,[1] and some were found in the literature, as is shown by the foot-notes. The couples are so written that the direction of the electromotive force is from left to right. The letter N preceding a chemical symbol is used throughout this article to represent a concentration of one equivalent (in grams) per liter of solution.

TABLE II.—THE ELECTROMOTIVE FORCE OF CERTAIN LIQUID-LIQUID COUPLES.

Couple.	E.m.f. in millivolts.	Couple.	E.m.f. in millivolts.
N/10 KCl | N/10 NaOH	21	N/10 KNO_3 | N/10 KOH	17
N/10 KCl | N/10 $Ba(OH)_2$	21	N/1 KCl | N/10 KOH	5
N/10 KCl | N/10 KOH	16	N/100 HCl | N/1 KCl	7
N/10 HBr | N/1 KCl	14	N/10 HCl | N/10 KCl[2]	28
N/10 NaCl | N/10 NaOH	18	N/10 HCl | N/10 NaCl[2]	33
N/10 KNO_3 | N/10 KCl	1	N/10 KCl | N/10 NaCl[2]	5
N/10 KNO_3 | N/10 $AgNO_3$	3	N/1 KCl | N/1 NaOH[3]	21
N/10 KNO_3 | N/1 KCl	1	N/10 HCl | N/100 HCl[4]	38
N/1 KCl | N/20 NaOH	3	N/100 HCl | N/10 KCl[4]	24
N/20 NaCl | N/1 KCl	2	N/10 KCl | N/1 KCl[5]	0.3
N/1 KCl | N/10 $Ba(OH)_2$	6	N/1 HCl | N/1 KCl[5]	28
N/10 KNO_3 | N/10 NaOH	23	N/1 HCl | N/10 HCl[5]	36

[1] Wied. Ann. 40, 561 (1890).

[2] Negbauer: Weid. Ann. 44, 737 (1891), Table 14.

[3] Smale, p. 611.

[4] Wilsmore, p. 303.

[5] Sauer.

4. COUPLES INVOLVING HALOGEN OR OXYGEN ELECTRODES.

As stated above, all of the couples involving halogen or oxygen electrodes needed in these calculations were not measured in combination with the "normal electrode." Some of them are derived from cells, the other electrode of which is hydrogen. The electromotive force data for the hydrogen electrode against solutions of various hydrogen-ion concentration have been critically considered by Wilsmore;[1] and his final values have therefore been adopted in these calculations. That for the hydrogen electrode against a normal hydrogen-ion solution is —277 millivolts; and those against various hydrochloric acid solutions, obtained in part by graphic interpolation, are as follows:

Solution.	Concentration.	E.m.f. × (—1).
HCl	N/1	271
"	N/10	217
"	N/20	200
"	N/100	161

The electromotive forces of the couples involving halogen or oxygen electrodes are given in millivolts in Tables III to VI. The values are the so-called absolute potentials, taking the value of the "calomel electrode" as —560 millivolts. A positive sign of the electromotive force of the electrode couple shows that the force acts in the direction from the electrode to the solution; a negative sign that it acts in the opposite direction. In the case of the liquid-liquid couples the value is written in the table with a negative sign when the direction of the electromotive force coincides with that of the cell, as in that case it has to be subtracted. When acting in the opposite direction, it is written with the positive sign. The chlorine and oxygen electrodes were saturated with these gases at atmospheric pressure; those of bromine or iodine, with these elements at the concentrations of their saturated solutions. The abbreviation N. E. is used to represent the so-called "normal electrode," N/1KCl, HgCl/Hg.

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[1] Z. physik. Chem. 35, 302; 36, 92 (1900).

TABLE III.—COUPLES INVOLVING THE CHLORINE ELECTRODE ($Pt+Cl_2$)

Temp.	Solution.	E.m.f. of chlorine couple ×(—1).	Cell measured.	E.m.f. of cell.	E.m.f. of other couple ×(—1).	E.m.f. of liquid-liquid couple.	Reference to cell measurement.
17°	N/1 HCl	1612[1]	H_2 | N/1 HCl | Cl_2	1341	271	0	Smale: Z. physik. Chem. 16, 563.
18°	N/1 HCl	1639	H_2 | N/1 HCl | Cl_2	1368	271	0	McIntosh, p. 285.
25°	N/1 HCl	1637	H_2 | N/1 HCl | Cl_2	1366	271	0	Müller.
18°	N/1 HCl	1652	N.E. | N/1 HCl | Cl_2	1064	560	+28	McIntosh, p 285.
Mean		1643					
18°	N/10 HCl	1703	H_2 | N/10 HCl | Cl_2	1486	217	0	McIntosh.
25°	N/10 HCl	1702	H_2 | N/10 HCl | Cl_2	1485	217	0	Müller.
18°	N/10 HCl	1712	N.E. | N/10 HCl | Cl_2	1138	560	+14	McIntosh, p. 285.
18°	N/10 HCl	1710	Cl_2 | N/1 HCl | N/10 HCl | Cl_2	103	1643	—36	Ibid., Table 8.
Mean		1707					
18°	N/100 HCl	1716	H_2 | N/100 HCl | Cl_2	1555	161	0	McIntosh.
25°	N/100 HCl	1707	H_2 | N/100 HCl | Cl_2	1546	161	0	Müller.
18°	N/100 HCl	1727	N.E. | N/100 HCl | Cl_2	1160	560	+ 7	McIntosh, p. 285.
..	N/100 HCl	1710	Cl_2 | N/10 HCl | N/100 HCl | Cl_2	41	1707	—38	Ibid., Table 8.
Mean		1715					
17°	N/1 KCl	1617	N.E. | N/1 KCl | Cl_2	1057	560	0	Smale, Table 5.
..	N/5 KCl	1666	....	....	...	..	Neumann.
17°	N/1 NaCl	1603	N.E. | N/1 NaCl | Cl_2	1048	560	—5	Smale, Table 5.

[1] Omitted in taking the mean.

The following table contains the means of the measurements made on the same couple.

TABLE IV.—FINAL VALUES OF COUPLES INVOLVING THE CHLORINE ELECTRODE ($Pt+Cl_2$) at 18°.

No.	Solution.	E.m.f. × (—1).	No.	Solution.	E.m.f. × (—1).
1	N/1 HCl	1643	6	N/1 KCl	1617
2	N/10 HCl	1707	7	N/2 KCl[1]	1636
3	N/20 HCl[1]	1709	8	N/5 KCl	1666
4	N/50 HCl[1]	1713	9	N/10 KCl[2]	1703
5	N/100 HCl	1715	10	N/1 NaCl	1603

It will be noticed that these potentials do not change with the concentration in accordance with the theory, from which the desirability of new measurements of the chlorine electrode in solutions of different chlorine-ion concentrations is evident. The deviations could of course be equalized upon a theoretical basis, but it is deemed best to base all these computations upon empirical data. It is probable that it is only the values for the 0.01 normal and the 0.02 normal hydrochloric acid that are seriously in error.[3]

[1] Interpolated graphically.

[2] Extrapolated graphically.

[3] It is a well-known fact that when chlorine is dissolved in water, it does not all remain in the form of molecular chlorine. Owing to the occurrence of the reaction,

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-,$$

the concentration of the chlorine ions is increased to a certain extent (Jakowkin: Z. physik. Chem. 29, 613 (1899)). It takes several hours, however, for this equilibrium to be established (Ibid., p. 625), and it is, therefore, doubtful whether, in measuring chlorine electrodes, the solution surrounding the electrode is allowed to stand in contact with the chlorine gas long enough to reach this state. Even granting that equilibrium is established, the following considerations will show that the effect on the potential for all couples used below would never exceed 7 millivolts. The solubility of chlorine in pure water is 0.089 mol. per liter (see Landolt-Börnstein-Meyerhoffer's tables, 3rd edition, p. 601, under column 1), of which 0.025 mol. is hydrolyzed (Boericke: Loc. cit., p. 63). According to the mass action law,

$$C_H \times C_{Cl} \times C_{HClO} = \text{const.} \times C_{Cl_2}.$$

But in saturated solutions, C_{Cl_2} is constant, and therefore

$$C_H \times C_{Cl} \times C_{HClO} = \text{const.} = (0.025)^3.$$

If the original concentration of hydrochloric acid is C_A, the new amount C of hydrochloric acid produced upon saturating the solution with chlorine is given by the equation

$$C(C_A + C)^2 = (0.025)^3.$$

Before giving the values of the couples involving the bromine electrode, a few prefatory remarks are necessary. When bromine is dissolved in a solution of hydrobromic acid or of a bromide, it adds itself to the bromide to form tribromide, in case only small quantities of bromine are added, while higher bromides are formed if the solution is saturated with bromine.[1] It is evident, therefore, that if we start with a normal solution of potassium bromide and saturate it with bromine, the solution no longer contains the usual quantity of bromide ions. There are in solution unknown amounts of KBr, KBr_3, KBr_5 and possibly higher bromides. Only the ions of the first of these compounds affect the electromotive force. Thus in combining with a bromine couple, a couple consisting of a silver electrode dipping in a normal solution of potassium bromide saturated with silver bromide, the former couple should theoretically consist of a bromine electrode in contact with a solution saturated with bromine and containing as many bromide ions per liter as the silver couple. In order to obtain such a bromine couple, a considerably stronger solution of potassium bromide would have to be started with. Measurements with such cells do not exist, but the electromotive forces of bromine electrodes dipping into solutions saturated with bromine and containing known amounts of bromide ions may be computed as follows. Let K be the equilibrium ratio for the reaction $Br_2 = 2Br^- + 2F^+$, defined by the equation $K = \frac{(C_{Br^-})_0^2}{(C_{Br_2})_0}$ and let (C_{Br^-}) and $(C_{Br_2}$[2]$)$ be the concentrations of bromide ions and free bromine molecules in any solution. The electromotive force of a bromine electrode against such a solution is then given by the formula

$$E = \frac{RT}{2F}\left[\log K - \log\frac{(C_{Br^-})^2}{C_{Br_2}}\right] = E_0 - \frac{RT}{2F}\log\left[\frac{(C_{Br^-})^2}{C_{Br_2}},\right]$$

When C_A is 0.1, C is 0.001, which is negligible. For 0.01 normal solution the correction amounts to 7 millivolts, but for the reason stated above, it is deemed best to leave this correction out of consideration.

In hydrochloric acid solutions a certain amount of HCl_3 is formed, which at 0° and in a 0.2 normal solution amounts to 0.8 per cent. (Jakowkin: *loc. cit.*, p. 635). The amount which would be formed at 17° is not known, but it could not introduce a serious error.

[1] Jakowkin: Z. physik. Chem. 20, 19 (1896).

[2] It may be well here to call attention to the fact that the C's are customarily given in mols. per liter.

where E_0, the so-called electrolytic potential, is the value of E when C_{Br}— and C_{Br_2} are both unity. From measurements in solutions where the concentrations C_{Br}— and C_{Br_2} could be computed the value of E_0 has been derived by two different observers,[1] the mean of whose values is $E_0 = -1.373$ volts at 25°. From this value, by means of the above formula, may be computed the potential of a bromine electrode dipping in a solution with any desired concentration of bromine molecules and bromide ions. A little consideration will show that the concentration of the bromine molecules here needed is substantially that of a saturated solution in pure water and that the concentration of the bromide ions involved is that which exists in water solutions of the bromide. In computing the following tables, the solubility of bromine in water at 25° is taken as 0.2125 mol per liter.[2] The potentials are computed for the electrode dipping in potassium bromide and also in hydrobromic acid, since the difference in dissociation between the salt and the acid causes a small variation in the potential.

TABLE V.—COUPLES INVOLVING THE BROMINE ELECTRODE ($Pt + Br_2$) at 25°.

Solution.	E.m.f. × (—1).	Solution.	E.m.f. × (—1).
N/1 KBr	1361	N/1 HBr	1359
N/2 KBr	1377	N/2 HBr	1375
N/5 KBr	1399	N/5 HBr	1397
N/10 KBr	1416	N/10 HBr	1414
N/20 KBr	1433	N/20 HBr	1431

In the case of the iodine electrode, considerations similar to those mentioned in the case of the bromine electrode apply. Here, however, the computation of the iodide ion concentrations is much simpler, as the ratio $\frac{KI_3}{KI+KI_3}$ for saturated solutions of iodine in potassium iodide has been found by Noyes and Seidensticker[3] to be almost exactly 0.5. From this datum Sammet[4] has computed the concentrations of the iodide ions in the solutions used by Crotogino, and has also duplicated his potential measurements. The maximum variation in these two sets of measure-

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[1] Boericke: Loc. cit., p. 71, found —1.375 volts; Sammet: Z. physik. Chem. 53, 681 (1905), found —1.371 volts.

[2] Boericke: Loc. cit.

[3] Z. physik. Chem. 27, 357 (1898).

[4] Loc. cit., Table 25.

ments is 1 millivolt. Plotting the logarithms of these iodide ion concentrations against the corresponding electromotive forces, a straight line is obtained from which may be read off the electromotive forces of iodine electrodes dipping into potassium iodide solutions saturated with iodine and containing the desired quantity of iodide ions. Table VI contains the results of this computation. The first and third columns give the strength of the solution which would have the stated voltage, if the iodine did not combine with the iodide. The actual solution is about twice as strong.

TABLE VI.—COUPLES INVOLVING THE IODINE ELECTRODE (Pt.+I_2) at 25°.

Solution.	E.m.f × (—1).	Solution.	E.m.f. × (—1).
N/1 KI	824	N/10 KI	883
N/2 KI	842	N/20 KI	901
N/5 KI	865		

There have been no measurements of the iodine electrode in solutions of hydriodic acid saturated with iodine. These values, however, would (as in the case of the bromine compounds) not be much different from the above. The only cause for difference would be in the unequal degree of dissociation of the salt and the acid.

For the potential of the oxygen electrode as derived from measurements of the hydrogen-oxygen cell, various values have been obtained. Thus for the electromotive force of that cell Smale first found about 1.08, Wilsmore[1] later 1.12, and Bose[2] very recently 1.14; and it has been clearly shown that the variation arises on the side of the oxygen, not the hydrogen electrode. In view of this uncertainty it has seemed best to adopt for the cell the value 1.22, which has just been derived independently through the study of chemical equilibria at high temperatures by three different investigators.[3]

The following table contains in the second column the values of the oxygen-liquid couples needed in these computations. The following columns give the data from which these are computed. The values of the electromotive force of the "cell measured" are taken from Smale's paper. By subtracting from this the electromotive force of the normal electrode (560 milli-

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[1] Loc. cit., p. 298.

[2] Z. physik. Chem. 38, 1 (1901).

[3] Lewis: This Journal, 28, 158 (1906); Haber: Z. Electrochem. 11, 834; Nernst: Ibid., 835.

volts) and adding that of the liquid-liquid couple, that of the hydrogen couple involved in the cell is obtained; and by subtracting this from 1220 that of the corresponding oxygen electrode results.

TABLE VII.—COUPLES INVOLVING THE OXYGEN ELECTRODE ($Pt + O_2$) at 17°.

Solution.	E.m.f. of couple × (−1).	Cell measured.	E.m.f. of of cell.	E.m.f. of liquid-liquid couple.	E.m.f. of hydrogen couple.
N/1 NaOH	710	| H_2 | N/1 NaOH | N.E.	1052	+21	513
N/KOH	710	| H_2 | N/1 KOH | N.E	1053	+16	509
Mean	710				
N/10 NaOH	760	| H_2 | N/10 NaOH | N.E.	1015	+ 6	461
N/10 KOH	750	| H_2 | N/10 KOH | N.E	1027	+ 5	472
Mean	755				
N/20 KOH or NaOH	768[1]				

5. ELECTROMOTIVE FORCE OF CELLS CONSISTING OF SATURATED SOLUTIONS OF CERTAIN HALIDES AND OXIDES AND ELECTRODES OF THEIR CONSTITUENTS.

The following series of tables shows the directly measured electromotive force of cells consisting in part of a metallic electrode and a saturated solution of one of its salts; the electromotive force of this electrode-liquid couple (called below the "first couple") together with the data involved in its derivation—the electromotive force of the other ("second") electrode-liquid couple and that of the liquid-liquid junction; and finally the electromotive force of a cell composed of the metallic electrode (M), the saturated solution of the salt (MA) and the non-metallic electrode (A), calculated by taking the algebraic difference between the electromotive force of the electrode-liquid couple just referred to, and that of the appropriate couple (with the same readily soluble electrolyte) given in Section 4. The first cell here referred to will be called the "measured cell" ("M. C.") and the second cell the "derived cell" ("D. C."). The cells are always written so that the direction of the current through the cell is from left to right.

The final mean value for each cell is obtained by averaging the values in the last column of each table, weights being assigned to each mean value equal to the number of measurements of the metallic couple. To change from volts to small calories, where one equivalent is involved, the factor $23{,}090 = \frac{96{,}600}{4.18}$ is employed.

---

[1] Extrapolated graphically.

TABLE VIII.—SILVER | SILVER CHLORIDE | CHLORINE.

			Electromotive force of					
Authority.	Cell measured = M. C.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Küster and Thiel	Ag ∣ AgCl, N/1 KCl ∣ N.E	25°	50	— 564	..	—514	—1617	1103
Luther, p. 648	Ag ∣ AgCl, N/10 HCl ∣ N/10 HCl, HgCl ∣ Hg	..	..	....	..	—554	—1707	1153
Zengelis	Ag ∣ AgCl, N/1 NaCl ∣ N.E.	..	35	— 560	+5	—520	—1603	1083
Zengelis	Ag ∣ AgCl, N/10 KCl ∣ N/10 KNO$_3$ ∣ N/10 AgNO$_3$ ∣ Ag	..	460	—1016[1]	—2	—558		
Goodwin, Table 27	Ag ∣ AgCl, N/10 KCl ∣ N/10 KNO$_3$ ∣ N/10 AgNO$_3$ ∣ Ag	25°	450	—1016	—2	—568		
Brönsted	Ag ∣ AgCl, N/10 KCl ∣ N/10 KCl, HgCl ∣ Hg	15°	43.7	— 614	..	—570		
Lovén	Ag ∣ AgCl, N/10 KCl ∣ N/10 KNO$_3$ ∣ N/10 AgNO$_3$ ∣ Ag	15°	443.3	—1016	—2	—575		
Abegg and Cox	N.E. ∣ N/10 KCl, AgCl ∣ Ag	25°	15	—564	..	—579		
					Mean =	—570	—1703	1133
							Final mean,	1123

Free energy of AgCl: —25,600 cal.

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[1] Zengelis: Loc. cit. This value is derived from the e.m.f. of the cell N.E. ∣ N/10 KNO$_3$ ∣ N/10 AgNO$_3$ ∣ Ag which is 0.458 volt or 0.456 corrected for junctions.

TABLE IX.—SILVER | SILVER BROMIDE | BROMINE.

			Electromotive force of					
Authority.	Cell measured.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Küster and Thiel	Ag $\mid$ AgBr, N/1 KBr $\mid$ N.E.	25°	198	— 564	..	—366	—1361	995
Zengelis	Ag $\mid$ AgBr, N/10 KBr $\mid$ N/10 KNO_3 $\mid$ N/10 $AgNO_3$ $\mid$ Ag	..	600	—1016	—2	—418		
Abegg and Cox	Ag $\mid$ AgBr, N/10 KBr $\mid$ N.E.	25°	133	— 564	..	—431		
Lovén	Ag $\mid$ AgBr, N/10 KBr $\mid$ N/10 KNO_3 $\mid$ N/10 $AgNO_3$ $\mid$ Ag	16°	601	—1016	—2	—417		
Goodwin	Ag $\mid$ AgBr, N/10 KBr $\mid$ N/10 KNO_3 $\mid$ N/10 $AgNO_3$ $\mid$ Ag	25°	599	— 101	—2	—419		
					Mean,	—421	—1416	995
Luther, p. 648	Ag $\mid$ AgBr, N/10 HBr $\mid$ N/10 HCl, HgCl $\mid$ Hg	..	...	....	..	—405	—1414	1009
							Final mean,	997

Free energy of AgBr: — 23,000 cal.

TABLE X.—SILVER | SILVER IODIDE | IODINE.

			Electromotive force of					
Authority.	Cell measured.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple,	First couple, M. C. and D. C.	Second couple, D. C.	D. C
Thiel	Ag | AgI, N/1 KI | N.E.	25°	422.8	—564	...	—141	—824	683
Zengelis	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	..	836	—1016	—2	—182		
Lovén	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	14.5°	816.5	—1016	—2	—202		
Goodwin	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	25°	814	—1016	—2	—204		
					Mean,	—196	—883	687
Danneel	Ag | AgI, N/10 HI | N/10 HI | H_2		23[1]	—217	0	—194	—883	689
							Final mean,	687

Free energy of AgI: —15,900 cal.

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[1] Interpolated graphically.

TABLE XI.—MERCURY | MERCUROUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of M. C.	 Second couple, M. C.	 Liquid-liquid couple.	 First couple, M. C. and D. C.	 Second couple, D. C.	 D. C.
Smale	N.E. | N/1 KCl | Cl$_2$	17°	1057	....	....	....	....	1057
Calame, p. 417	N.E | N/10 KCl, HgCl | Hg	..	56	—560	+0.3	—616.3		
Sauer	N.E. | N/10 KCl, HgCl | Hg	18°	51.4	—560	+0.3	—611.7		
					Mean,	—614	—1703	1089
Sauer	Hg | HgCl, N/1 HCl | N.E.	18°	32.3	—560	—28	—556		
Carveth	D.E.[1] | N/1 HCl, HgCl | Hg	..	557	0	0	—557		
					Mean,	—557	—1643	1086
Sauer	Hg | HgCl, N/10 HCl | N/10 KCl, HgCl | Hg	18°	28.6	—614	—28	—613		
Sauer	Hg | HgCl, N/1 HCl | N/10 HCl, HgCl | Hg	18°	98.8	—557	—36	—620		
Carveth	D.E. | N/10 HCl, HgCl | Hg	..	605	0	0	—605		
					Mean,	—619	—1707	1088
Immerwahr	N.E. | N/1 KNO$_3$, N/20 KCl, HgCl | Hg	..	76.8	—560	0	—637	—1709	1072
							Final mean,	1083

Free energy: —49,400 cal.

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[1] "Dropping Electrode."

TABLE XII.—MERCURY | MERCUROUS BROMIDE | BROMINE.

Authority.	Cell measured.	Temp.	Electromotive force of M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Behrend	Hg | HgBr, N/10 KBr | N/10 KCl, HgCl | Hg	ab't 20°	131	—614	0	—483		
Goodwin, Table 33	Hg | HgBr, N/10 KBr | N/10 KCl, HgCl | Hg	15–18°	133.8	—614	0	—480		
					Mean,	—481	—1416	935
Immerwahr	Hg | HgBr, N/1 KNO$_3$ N/20 KBr | N.E.	....	39	—560	0	—521	—1433	912
							Final mean,	927

Free energy: —42,800 cal.

TABLE XIII.—MERCURY | MERCUROUS IODIDE | IODINE.

Authority.	Cell measured.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Behrend	Hg | HgI, N/10 KI | N/10 KCl, HgCl | Hg	ab't 20°	322	—614	0	—292	—883	591
Immerwahr	Hg | HgI, N/1 KNO$_3$, N/20 KI | N.E.	....	226.4	—560	0	—334	—901	567
							Final mean,	579

Free energy: —26,800 cal.

TABLE XIV.—COPPER | CUPROUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Immerwahr[1]	Cu | CuCl, N/1 KNO$_3$, N/20 HCl | N.E.	..	95	—560	0	—465	—1709	(1244)
Luther and Wilson	Cu | CuCl, N/20 KCl | N.E.	25°	..	—564	..	—491	—1709	1218
							Final mean,	1218

Free energy: —27,800 cal.

TABLE XV.—COPPER | CUPROUS BROMIDE | BROMINE.

Immerwahr	Cu | CuBr, N/1 KNO$_3$, N/20 KBr | N.E.	..	156	—560	0	—404		
Luther and Wilson	Cu | CuBr, N/20 KBr | N.E.	25°	..	—564	..	—410		
Bodländer and Storbeck	Cu | CuBr, N/20 KBr | N.E.	..	..	...	..	—402		
					Final mean,	—405	—1433	1028

Free energy: —23,700 cal.

TABLE XVI.—COPPER | CUPROUS IODIDE | IODINE.

Immerwahr	Cu | CuI, N/1 KNO$_3$, N/20 KI | N.E.	..	373	—560	0	—187		
Bodländer and Storbeck	Cu | CuI, N/20 KI | N/20 KBr, CuBr | Cu	..	225.8	—405	0	—179		
					Final mean,	—183	—901	718

Free energy: —16,600 cal.

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[1] Omitted. See Luther: Z. physik. Chem. 36, 385 (1901).

TABLE XVII.—THALLIUM | THALLOUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Neumann	Tl | Tl sat. in H_2O[1] | N.E.	..	..	..	..	151	—1715	1866
Goodwin, Table 2	Tl | TlCl, N/5 KCl | N/5 KNO_3, TlCl | Tl	25°	59.0	+151	+1	211	—1666	1877
Goodwin, Table 2	Tl | TlCl N/10 KCl | N/10 KNO_3,TlCl | Tl	25°	44.2	+151	+1	196	—1703	1899
Goodwin, Table 2	Tl | TlCl N/20 KCl | N/20 KNO_3, TlCl | Tl	25°	30.1	+151	+1	182	—1709	1891
							Final mean,	1883

Free energy: —43,200 cal.

TABLE XVIII.—THALLIUM | THALLOUS BROMIDE | BROMINE.

Authority.	Cell measured.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Goodwin, Table 34	Tl | TlBr, N/5 KBr | N/5 KCl, TlCl | Tl	25	101.3	+211	0	312	—1399	1711
Goodwin, Table 34	Tl | TlBr, N/10 KBr | N/10 KCl, TlCl | Tl	25	100.7	+196	0	297	—1416	1713
Goodwin, Table 34	Tl | TlBr, N/20 KBr | N/20 KCl, TlCl | Tl	25	99.1	+182	0	281	—1433	1714
							Final mean,	1713

Free energy: —39,600 cal.

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[1] Concentration of ions is 0.01 normal. See Wilsmore, Loc. cit.

TABLE XIX.—LEAD | LEAD CHLORIDE | CHLORINE.

			Electromotive force of					
Authority.	Cell measured.	Temp.	M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Neumann	Pb $\mid$ $PbCl_2$ sat. in H_2O[1] $\mid$ N.E.	..	..	....	..	—95	—1709	1614
Zengelis	Pb $\mid$ $PbCl_2$, N/10 KCl $\mid$ N.E.	..	546	—560	0	—14	—1703	1689
Immerwahr	Pb $\mid$ $PbCl_2$, N/2 KCl, N/1 KNO_3 $\mid$ N.E.	..	514	—560	0	—46	—1636	1590
Immerwahr	Pb $\mid$ $PbCl_2$, N/20 KCl, N/1 KNO_3 $\mid$ N.E.	..	482.6	—560	0	—77	—1709	1632
Immerwahr	Pb $\mid$ $PbCl_2$, N/20 HCl, N/1 KNO_3 $\mid$ N.E.	..	484.6	—560	0	—75	—1709	1634
							Final mean,	1632

Free energy: —74,800 cal.

TABLE XX.—LEAD | LEAD BROMIDE | BROMINE.

Zengelis	Pb $\mid$ $PbBr_2$, N/10 KBr $\mid$ N.E.	..	561	—560	0	1	—1416	1417
Immerwahr	Pb $\mid$ $PbBr_2$, N/20 KBr, N/1 KNO_3 $\mid$ N.E.	..	493.0	—560	0	—67	—1433	1366
							Final mean,	1391

Free energy: —64,200 cal.

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[1] Concentration of lead ions is 0.04 N (Wilsmore, l.c.). Attention is here called to the fact that Wilsmore used the word "normal" in the sense of "molal." This makes a correction necessary for the electrolytic potentials as given by him in the case of all except univalent metals. For bivalent metals the correction amounts to 8 millivolts. This has been overlooked by ertain authors who have copied his data.

Table XXI.—Lead $\mid$ Lead Iodide $\mid$ Iodine.

Authority.	Cell measured.	Temp.	Electromotive force of M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Zengelis	$Pb \mid PbI_2$, N/10 KI $\mid$ N.E.	..	617	—560	0	+57		
Findlay	$Pb \mid PbI_2$, N/10 NaI $\mid$ N.E.	25°	(574)[1]	—564	0	+10		
						Mean, 33	—883	916
Findlay	$Pb \mid PbI_2$, N/20 NaI $\mid$ N.E.	25°	(556[1])	—564	0	— 8		
Immerwahr	$Pb \mid PbI_2$, N/1 KNO_3,N/20 KI $\mid$ N.E.		546.0	—560	0	—14		
						Mean, —11	—901	890
							Final mean,	903

Free energy: —41,700 cal.

[1] Not given in the original paper, but computed from the value of each couple.

TABLE XXII.—MERCURY | MERCUROUS OXIDE | OXYGEN.

<table>
<tr><th rowspan="2">Authority.</th><th rowspan="2">Cell measured.</th><th rowspan="2">Temp.</th><th colspan="6">Electromotive force of</th></tr>
<tr><th>M. C.</th><th>Second couple, M. C.</th><th>Liquid-liquid couple.</th><th>First couple, M. C. and D. C.</th><th>Second couple, D. C.</th><th>D. C</th></tr>
<tr><td>Wilsmore</td><td>Hg | Hg_2O, N/1 KOH | N.E</td><td>25°</td><td>..</td><td>..</td><td>..</td><td>—415</td><td></td><td></td></tr>
<tr><td>Smale, p. 611</td><td>Hg | Hg_2O, N/1 NaOH | N.E</td><td>17°</td><td>129.6</td><td>—560</td><td>+20.5</td><td>—410</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>Mean,</td><td>—413</td><td>—710</td><td>297</td></tr>
<tr><td>Behrend</td><td>Hg | Hg_2O, N/10 NaOH | N/10 KNO_3 | N/10 KCl, HgCl | Hg</td><td>ab't 20°</td><td>130</td><td>—614</td><td>+22</td><td>—462</td><td>—760</td><td>300</td></tr>
<tr><td>Behrend</td><td>Hg | Hg_2O, N/10 KOH | N/10 KNO_3 N/10 KCl, HgCl | Hg</td><td>ab't 20°</td><td>143</td><td>—614</td><td>+16</td><td>—455</td><td>—750</td><td>290</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>Final mean,</td><td>296</td></tr>
</table>

Free energy: —13,400 cal.

TABLE XXIII.—SILVER | SILVER OXIDE | OXYGEN.

<table>
<tr><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></tr>
<tr><td>Abegg and Cox</td><td>N.E. | N/10 $Ba(OH)_2$, Ag_2O | Ag.</td><td>25°</td><td>111</td><td>—564</td><td>—6</td><td>—669</td><td>—760</td><td>91</td></tr>
</table>

Free energy: —3,910 cal.

In the case of chlorides of the type MCl the free energy of one molecule is calculated by the expression—(EF—0.5 RT) which is equal in calories to—(23,090E—288), while for bromides and iodides the term 0.5 RT drops out. For chlorides of the type MCl_2 the free energy of one mol. is—(2EF—RT) while in the case of bromides and iodides of this type the term RT is again omitted. For oxides of the types MO and M_2O the free energy is— (2EF—0.5 RT).

6. COMPUTATION OF THE FREE ENERGY FROM SOLUBILITY AND ELECTROLYTIC POTENTIALS.

The free energy of one mol consisting of N equivalents, of an n-ionic solid compound may also be calculated from the electrolytic potentials E_C and E_A of its elements (of which let N mols be gaseous), and from the solubility s of the compound (expressed in equivalents per liter and regarded as completely ionized) by the following formula, which in somewhat different form was first derived by Bodländer:[1]

$$—F=(E_C—E_A)NF—nRT \log s—NRT.$$

It is, therefore, of interest to compare the results obtained in this way with those computed above directly from decomposition-potentials of the saturated solutions.

For this purpose the electrolytic potentials for the metals are taken from Wilsmore's paper. With respect to the non-metals it is important to note that in the case of all elements whose concentrations in the electrode can be varied, such as the halogens

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[1] Loc. cit. The above formula may also be deduced by the following reversible process in which one mol of an n-ionic salt consisting of N equivalents is formed from its elements, of which N mols may be gaseous. Make use of a cell consisting of the elementary substance as electrodes dipping into a normal solution of the corresponding ions. Let this cell act reversibly until N equivalents of the elementary substances have gone into solution as ions, at the same time adding to the solution reversibly the quantity of water necessary to keep the concentration constant. The work done by the cell in this process is $(E_C - E_A)NF - NRT + nRT$. Now allow the salt to change its concentration to that corresponding to its solubility S (by cutting off the quantity of solution which contains one mol and diluting it); assuming it is completely dissociated in both solutions, the work done by the system in this process is $nRT \log 1/S$. Now force the salt out of solution by means of a semi-permeable piston, in which the work done by the system is $-nRT$. The total work done by the system is therefore $(E_C - E_A)\, NF + nRT \log 1/S - NRT$.

and oxygen, there are two kinds of specific electrolytic potentials—one, where the solution is saturated with respect to the element in question, the other, where the solution is molal with respect to it, the solution being molal with respect to the ions of the element in both cases.[1] It is evident the former is the proper one to employ in these computations. For computing the electrolytic potential of chlorine Sullivan's[2] value of the equilibrium ratio for the reaction $Cl_2 = 2Cl^- + 2F^+$ has been adopted. The value of the solubility of chlorine in pure water is 0.089 mol per liter at 25°. It would, however, be less in a solution normal with respect to chloride ions. There is good reason for the assumption that in a normal potassium chloride solution the solubility at 25° would be only 81 per cent. of the above amount,[3] and for a solution normal with respect to chloride ions, the reduction in solubility would probably not be much greater. Therefore, the solubility is taken as 0.072 mol per liter. The resulting value of the electrolytic potential differs by 1 millivolt from the value computed by Haber.[4]

In computing the electrolytic potential of bromine with respect to a solution saturated with bromine molecules, the solubility is taken the same as in pure water, 0.2125 mol per liter at 25°. By means of this datum the electrolytic potential with respect to a solution saturated with bromine molecules is computed from the electrolytic potential used above with respect to a solution molal with bromine molecules. The electrolytic potential of iodine in a solution saturated with respect to iodine molecules may be obtained exactly as the values in Table VI, and therefore depends on Crotogino's measurements.

The following table gives the results of this computation.

TABLE XXIV.—THE ELECTROLYTIC POTENTIALS OF THE HALOGENS IN SOLUTIONS SATURATED WITH THEM AT 25°.

E_{Cl_2}	—1.643
E_{Br_2}	—1.353
E_{I_2}	—0.817

The values of the solubilities are taken from the third edition of Landolt-Börnstein-Meyerhoffer's tables, and only those are used

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[1] See Haber: Z. Elektrochem. p. 1047.

[2] Z. physik. Chem. 28, 523 (1899), $\log_{10} K = 56.756$.

[3] Jakowkin: Z. physik. Chem. 29, 637 (1899); Boericke: Loc. cit., p. 63.

[4] Loc. cit., p. 1047.

which are not based on measurements used above, so as to avoid working in a circle.

The values of the free energy computed in this way are given in column 4 of Table XXVIII.

7. THE FREE ENERGY OF MERCURIC CHLORIDE, BROMIDE, AND IODIDE.

If the equilibrium between a metal and two of its halides in different states of oxidation is known, the free-energy change attending the decomposition of the lower halide into the higher halide and the metallic element may be computed, and this combined with the free energy of the lower halide, gives that of the higher one. The necessary data exist in the case of the mercury halides, since the concentration of each mercuric halide (as such) in equilibrium with the corresponding solid mercurous halide and mercury has been indirectly determined by Sherrill.[1] If that concentration be designated by C and the solubility of the mercuric halide (regarded as nonionized and unassociated) by S, then the work producible by the reaction

$$Hg_2X_2(\text{solid}) = Hg + HgX_2(\text{solid})$$

may be readily shown[2] to be $RT \log_e C/S$. And evidently the algebraic sum of this quantity of work and of that attending the production of one formula weight of Hg_2X_2 out of its elements is the free-energy decrease attending the formation of one formula weight of HgX_2 out of its elements.

The values of the quantities C and S given by Sherrill, of the calculated quantity of work $RT \log_e C/S$, and of the free energy in calories of the mercuric halides are given in the following table.

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[1] Z. physik. Chem. 47, 103 (1904).

[2] In a reaction mixture consisting of mercury and solid mercurous halide in equilibrium with an aqueous solution of mercuric halide of concentration C, let one formula weight of solid Hg_2X_2 decompose into mercury and (dissolved) HgX_2, the latter being simultaneously removed at the same concentration into pure water through a wall permeable for it alone. The work produced hereby is RT. Now concentrate the HgX_2 solution so obtained till its concentration becomes S, that of a saturated solution: the work produced is $RT \log_e C/S$. Finally force the salt out of the solution in the solid state: the work produced is $-RT$. The total work is therefore $RT \log_e C/S$.

TABLE XXV.—FREE ENERGIES OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

Substance.	$C \times 10^6$ in mols per l.	$S \times 10^3$ in mols per l.	$RT \log_e C/S$.	Free energy $\times (-1)$.
$HgCl_2$	2.9	260.0	—6750	42600
$HgBr_2$	2.4	17.0	—5250	37300
HgI_2	4.0	0.13	—2060	24100

8. THE FREE ENERGY OF WATER, AMMONIA, HYDROGEN CHLORIDE, AND HYDROGEN BROMIDE.

Hydrogen | Liquid Water | Oxygen.

As stated above, the best value for the electromotive force of this cell seems to be 1.22 volts at about 20°. The corresponding value of the free energy of one mol of water calculated by the equation $F = -[2\mathrm{EF} - 1.5RT]$ is 55,500 calories.

Hydrogen | Hydrochloric Acid | Chlorine.

The free energy formula $F = -(\nu\mathrm{EF} + \Delta NRT)$, given in Section 1 of this article that applies to a solid in contact with its saturated solution applies equally well to a gas in equilibrium with its solution (it being understood that ΔN represents the increase in the number of mols of gas attending the reaction). Thus, if we have a hydrogen and a chlorine electrode in normal hydrochloric acid, the electromotive force of this cell would give the free energy of hydrochloric acid at a pressure equal to its partial pressure over its normal solution, referred to hydrogen and chlorine at atmospheric pressure. The term ΔN becomes zero, as there are as many mols of gas before as after the reaction has taken place. If, however, we wish to know the free energy of hydrochloric acid at atmospheric pressure, referred to hydrogen and chlorine at atmospheric pressure, then the free energy computed from the voltage must be diminished by $RT \log_e 760/p$, where p is the partial pressure in millimeters of mercury of hydrochloric acid over the solution in question. The necessary measurements of vapor-pressure and electromotive force have been made for hydrochloric and hydrobromic acids, but not for hydriodic acid.

Dolezalek[1] has measured the cell $H_2 \mid HCl \mid Cl_2$ at 30° and at different concentrations. He has also measured the partial pressures of hydrochloric acid at the same temperature, for different concentrations. The following table contains these results, and in the last column the free energy computed from them.

[1] Z. physik. Chem. 26, 321 (1898).

TABLE XXVI.—DATA FOR HYDROCHLORIC ACID AND ITS FREE ENERGY.

Equivalents per liter.	Partial pressure in mm. of Hg 30°.	E.m.f. in volts.	Free energy × (—1) of one mol at 30°.
4.98	0.24	1.190	22,800
6.43	0.69	1.147	22,400
11.20	134.0	1.005	22,200
11.62	189.0	0.999	22,300
12.14	313.0	0.981	22,100
12.25	337.0	0.974	22,000

The average value is 22,300 calories ±0.5 per cent., at 30°. The heat of the reaction ($-U$) is 22,000[1] calories at 18°, and varies very slightly with the temperature. It would be practically the same at 30°. The temperature coefficient of the free energy F at 30° is then $\frac{dF}{dT}=\frac{F-U}{T}=1.07$ calories per degree. The free energy at 18° would then be only 1.8 calories less than that at 30°. This correction is, therefore, negligible.

Hydrogen | Hydrobromic Acid | Bromine.

Measurements of the above cell have been made by Bodenstein and Geiger[2] at 30°, as well as of the vapor-pressures of the hydrobromic acid over the solutions and of the hydrogen and the bromine. The bromine couple was not saturated with bromine. The electromotive force of this cell gives the free energy of hydrobromic acid at the partial pressure measured, formed from gaseous bromine and hydrogen at the measured pressures.

If we start with gaseous bromine at atmospheric pressure (assuming this degree of supersaturation could be realized), this must be expanded to the pressure at which it exists in the cell. The work done by the system will be $0.5\,RT \log_e \frac{760}{P_{Br_2}}$ for one-half of a mol. Allowing the hydrogen to change from atmospheric pressure to that measured, the work done by the system will be $0.5\,RT \log_e \frac{760}{P_{H_2}}$. Now compressing the acid to atmospheric pressure, the work done by the system will be $-RT \log_e \frac{760}{P_{HBr}}$. Hence the free energy is given by the formula:

$$-F = E \times 23090 + 0.5\,RT \log_e \frac{(P_{HBr})^2}{(P_{Br_2})(P_{H_2})}.$$

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[1] Ostwald: Lehrbuch allg. Ch. 2te Aufl. Bd. II, 1, p. 103.

[2] Z. physik. Chem. 49, 70 (1904).

The following table gives the data for this computation, the final column containing the free energy itself.[1]

TABLE XXVII.—DATA FOR HYDROBROMIC ACID AND ITS FREE ENERGY.

Partial pressure in mm. of mercury.				
HBr.	Br_2.	H_2.	E.m.f. in volts.	Free energy $\times(-1)$.
12.0	0.682	742.5	0.573	12850
2.25	1.509	753.6	0.625	12800
1.19	1.448	760.6	0.636	12680

The average value is 12,800 calories at 30°. The difference in the heat capacities at constant volume of one mol of hydrobromic acid and of its constituents is 1.06 calories.[2] The heat of the reaction is, therefore, practically the same for 30°. In order to get the free energy at 18° we may substitute the known values in the integrated Second Law equation given below (see under Ammonia). This gives at 18° F = —11950 calories.

Hydrogen | Ammonia | Nitrogen.

The cell $Pt+H_2$ | solid NH_4NO_3+solution of NH_4NO_3 in NH_3 | $Pt+N_2$ is stated by Baur to be reversible and to have at —10° an electromotive force of 590 millivolts.[3] The partial pressure p of the ammonia over this mixture has been found to be 240 mm. at —10.5°.[4] Now the free energy (F) of one mol of gaseous ammonia at atmospheric pressure referred to its elements at atmospheric pressure (p_0) is given by the expression,

$$-F = 3\text{EF} - RT + RT \log_e p/p_0,$$

from which by substituting the above values one finds at —10° F = —39,700 calories.

In order to obtain from this the free energy at 18° we may employ the Second Law equation $\frac{dF}{dT} = \frac{F-U}{T}$, which, integrated under the assumption that the energy increase (U) attending the reaction is constant, gives $\frac{F_2}{T_2} - \frac{F_1}{T_1} = -U\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$. U, however, has the value —11,420 calories at 18° and —11,280 calories at —10°, or an average value of —11,350 calories.[5]

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[1] Subsequently to sending this article to the Journal, it was found that calculations of the free energy of hydrochloric and hydrobromic acids had previously been published by Haber in his book "Thermodynamik technischer Gasreaktionen."

[2] Obtained from Landolt-Börnstein-Meyerhoffer's tables.

[3] Baur: Z. anorg. Chem. 29, 305 (1902).

[4] Kuriloff: Z. physik. Chem. 25, 108 (1898).

[5] Ostwald: Loc. cit., p. 139.

Putting $F_1 = -39,700$, $T_1 = 263$ and $T_2 = 291$ we find for F_1 (which is the free energy of one mol gaseous NH_3 at 18° and one atmosphere pressure) the value of —45,200 calories.

This result may be compared with that obtained by using the equilibrium constant of the reaction in question recently obtained for the temperature 1020° by Haber and Van Oordt.[1] At this temperature, this constant, which is defined by the equation

$$K = \frac{(P_{N_2})^{0.5} \quad (P_{H_2})^{1.5}}{(P_{NH_3})},$$

has, when the pressure is expressed in atmospheres, the value 2706. From this value the work producible by the reaction

$$0.5N_2 + 1.5H_2 = NH_3$$

when it takes place from left to right and when each gas is at atmospheric pressure is calculated by the equation given in Section I of this article to be —23,000 calories. By means of the heat of reaction and heat capacity data cited by the authors and the integrated form of the Second Law equation given by them the work produced may be computed for any other temperature. For 18° it is found to be +5100. Hence we have for the free energy of one mol of ammonia, $F = -5100$ calories.

This result is evidently utterly inconsistent with the value deduced from potential measurements. The most probable explanation seems to be that there is an error in the interpretation of the potential values arising from the fact that the potential observed was not determined by the solution-tendency of nitrogen at all, but by some other reaction in the solution. Nitrogen is a very inert gas, especially at low temperatures; and therefore this seems a reasonable explanation. There does not seem to be any corresponding possibility of a large error in the computation involving the equilibrium constant, and it is probable that the value of the free energy deduced therefrom is at least an approximate one. Both are given in Table XXIX.

9. SUMMARY OF THE RESULTS.

The results of the above-described computations as well as certain other related data are presented in Table XXVIII. Column 2 contains the free energies of the chlorides referred to gaseous chlorine at atmospheric pressure. These values are here collected from the various preceding tables. By adding $N R T$ to these

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[1] Z. anorg. Chem. 44, 341 (1905).

the values in column 3 for the chlorides are obtained, which show what their free energies would be if the chlorine were liquid or solid at the temperatures in question. The previously computed free energies of bromides and iodides are also given in this column. The free energies computed from solubilities are given in column 4. The values that deviate widely from those in column 3, which is the case with the most difficultly soluble compounds where the error in determining the solubility is large, are placed in brackets. The next three columns contain the values of the total energies, all of which are taken from the third edition of Landolt-Börnstein-Meyerhoffer's Tables. Column 5 contains the total energy of the chlorides with respect to gaseous chlorine. From this value the heat of vaporization (2200 calories for one atomic weight)[1] has been subtracted, and the so obtained total energies referred to liquid chlorine are given in column 6, as are also the total energies of the bromides referred to liquid bromine. Column 7 contains the total energies referred to the halogens as solids. In the case of the bromides, the heat of fusion of bromine at its melting-point —7.3° (1300 calories) has been subtracted from the value given in column 7 to get the total energy referred to solid bromine. The heat of fusion of chlorine has not been determined, but as an approximate basis of comparison the heat of fusion has been assumed identical with that of bromine, which seems justifiable since bromine and iodine differ but little. These values are of course fictitious ones, since solid chlorine and bromine cannot exist at 18°; they are, therefore, enclosed in parentheses. They represent what the total energies would be if the solid elements were superheated to 18° and there had the same heat of fusion as at lower temperatures. In the case of the mercury halides, the total energy is given in the seventh column with respect both to solid and to liquid mercury, the heat of fusion (600 calories) being assumed identical with that at the melting-point.

Column 8 contains the ratio of the free to the total energies referred to the elements in the solid state, while column 9 gives the same ratio for the elements in the ordinary state. (For the chlorides this is the ratio of values in column 2 to those in column

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[1] It is not clear whether this value which is cited as a private communication from Knietsch includes the external work, but this would make a difference of only about 300 cal.

Table XXVIII.—The Free and Total Energies of the Solid Halides of Silver, Mercury, Copper, Thallium, and Lead at about 18°.

	Free energy × (−1).			Total energy × (−1).			Ratio of free to total energy.		
Formula of compound. 1.	Halogen gaseous at atmos. pres. 2.	Halogen liquid or solid. 3.	Halogen in usual state computed from solubilities. 4.	Halogen gaseous. 5.	Halogen liquid. 6.	Halogen solid. 7.	Elements solid. 8.	Elements in usual state. 9.	Solubility at 20° in equivalents per liter. 10.
AgCl	25600	25900	26800[6]	28900	26700	(25400)	1.02	0.89	1.06×10^{-5}
AgBr	....	23000	23900	....	23400[1]	(22100)	1.04	0.98	5.1×10^{-7}
AgI	....	15900	[26300]	....	....	14200[1]	1.12	1.12	$1\ 5\times10^{-8}$
CuCl	27800	28100	....	33800	31600	(30300)	0.93	0.82	......
CuBr	....	23700	....	....	25000	(23700)	1.00	0.95	......
CuI	....	16600	....	....	....	16600	1.00	1.00	......
TlCl	43200	43500	43700	48300	46100	(44800)	0.97	0.89	1.39×10^{-2}
TlBr	....	39600	39700	....	41300	(40000)	0.99	0.96	1.64×10^{-3}
TlI	....	....	29900	....	....	30200	0.99	0.99	1.92×10^{-4}
Hg_2Cl_2	49400	50000	52100	62000	57600	(55000)[3] (53800)[4]	0.93	0.80	1.6×10^{-6}
Hg_2Br_2	....	42800	42900	....	49000[3]	(46400)[3] (45200)[4]	0.95	0.88	1.4×10^{-7} [2]
Hg_2I_2	....	26800	[46400]	....	....	28800[3] (27600)[4]	0.97	0.93	6.1×10^{-10} [2]
$HgCl_2$	....	43200[5]	42600	52600	48200[3]	(45600)[3] (45000)[4]	0.96	0.81	5.26×10^{-1} [2]
$HgBr_2$	....	....	37300	....	40500[3]	(37900)[3] (37300)[4]	1.00	0.92	3.4×10^{-2} [2]
HgI_2 (red)	....	....	24100	....	....	25100[3] (24500)[4]	0.98	0.96	2.6×10^{-4} [2]
$PbCl_2$	74800	75400	74300	82700	78300	(75700)	1.00	0.90	7.14×10^{-2}
$PbBr_2$	....	64200	62300	....	64500	(61900)	1.04	1.00	4.64×10^{-2}
PbI_2	....	41700	42300	....	....	39800	1.05	1.05	2.98×10^{-3}

[1] Berthelot's value. [2] At 25°. [3] Mercury liquid. [4] Mercury solid. [5] Computed from column 4.

[6] Using Lewis' recent determination of the electrolytic potential of silver, the values for the chloride, bromide and iodide are 26500, 23300 and [27000]. See this Journal, 28, 158 (1906).

5); column 10 gives the values of the solubilities used in computing column 4.

All energy values are in gram-calories, are for one formula weight of salt as shown in the first column, and are based on the convention that the energy of the elements (considered gaseous, liquid or solid as shown) is zero. The chlorine when gaseous is at atmospheric pressure.

Table XXIX contains the results for other compounds than the halides, and needs no explanation.

TABLE XXIX. — THE FREE AND TOTAL ENERGIES OF THE OXIDES OF SILVER AND MERCURY, OF WATER, AMMONIA, HYDROCHLORIC AND HYDROBROMIC ACIDS AT ABOUT 18°.

Compound.	Free energy ×(−1).	Total energy ×(−1).	Ratio of free to total energy.
Hg_2O	13400	22200	0.60
Ag_2O	3900	5900	0.66
Ag_2O[1]	3310	5900	0.56
H_2O (liquid)	55500	67600	0.82
H_2O[2]	53800	57500	0.93
HCl[2]	22300	22200	1.01
HBr[2]	11950	8400	1.42
NH_3[2] (Baur)	45200	11400	4.00
NH_3[2] (Haber)	5100	11400	0.45

10. DISCUSSION OF THE RESULTS.

First may be noted the good agreement between the free energy values of column 2 or 3 and those of column 4 in Table XXVII, the differences between which seldom exceed 4 per cent. The two series of values are based upon independent data, except that the same measurements of potentials of the halogen electrodes against halide solutions are to a great extent involved in both calculations. Except with respect to this last factor, the agreement is therefore a confirmation of the accuracy of the results. To this agreement there are two pronounced exceptions, namely in the case of the iodides of silver and mercurous mercury, where the free energies calculated from solubilities and electrolytic potentials against normal solutions of the ions exceed

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[1] This is the free energy computed from Lewis' recent value of the decomposition-pressure of silver oxide. (See this Journal, 28, 158, (1906)).

[2] Compounds gaseous at atmospheric pressure. In the case of water this condition is, of course, unrealizable at 18°, but the computed values represent, nevertheless, approximately what the energies would be if water-vapor were supersaturated to that extent.

those calculated from the electromotive force of cells with the salts present as solid phases by 65 and 73 per cent. The explanation of this extraordinary disagreement is by no means obvious; it can not be due to an error in the electrolytic potential of the iodine electrode, for this is in substance common to both calculations, nor to one in that of the silver or mercury electrode, for this would have produced disagreement also in the cases of the chlorides and bromides of these elements; it is moreover difficult to believe it is due to an error in the potentials of the metals against the saturated solutions, since these values are based on fairly concordant measurements by different observers —five in the case of silver iodide, two in the case of mercurous iodide (see Tables X and XIII); and finally it can hardly be due to error in the solubilities, for in order to give values of the free energy identical with those computed from the potentials against the saturated solutions it would be necessary to assume for these two iodides solubilities (1.1×10^{-4} for AgI, 7.8×10^{-5} for Hg_2I_2) greater than those for the corresponding chlorides (1.06×10^{-5} for AgCl, 1.6×10^{-6} for Hg_2Cl_2) which is well-known not to be the case. The most probable explanation of the discrepancy would seem to be that there exists in the solutions of these iodides complex ions which make the computation from their solubilities uncertain. However this may be, from every point of view the free energy computed in the other way seems more reliable: first, because it does not involve any theoretical assumptions; second, because its values correspond for these two salts far better with those of the total energy (see below); and third, because they fall in line with those for the corresponding chlorides and bromides. Another point worthy of mention in connection with the two sets of free energy values is that in case of mercurous chloride and bromide these agree more closely when the salts are assumed to be tri-ionic ones of the formula $(Hg_2)Cl_2$ or $(Hg_2)Br_2$ rather than di-ionic ones of the formula HgCl or HgBr. Thus the values calculated from the solubilities under the former assumption are (as given in the table) 52,100 for the chloride, 42,900 calories for the bromide, and under the latter assumption 60,600 and 53,400 calories respectively, while the values computed from the potentials against the saturated solutions are 49,400 and 42,800 calories respectively.

In regard to the magnitude of the free energies of the different compounds the following approximate regularities will be seen to exist.

(1) In the case of these solid halides, the chloride has a free energy uniformly greater than that of the corresponding bromide by from 2500 to 5500 calories per equivalent, and the bromide has a free energy greater than that of the corresponding iodide by 7000 to 11,000 calories per equivalent.

(2) The corresponding halides of mercurous mercury, silver, and cuprous copper have free energies which differ from each other by less than 3500 calories per equivalent, but which increase slightly in every case in the order mercury, silver, and copper.[1]

The most important general conclusion to be drawn from these results relates, however, to the connection between the free and total energies. It will be seen from column 8 of Table XXVIII that *the ratio of the free to the total energy of these solid salts when these energies are referred to those of the elements in the solid state as zero does not differ from unity by more than 7 per cent.*, except in the single instance of silver iodide. This principle, which is of great importance since it enables for approximate purposes the usually well-known heat of formation to be employed in the place of the often unknown free energy in the study of the equilibrium of reactions involving solid substances, has not previously been so extensively tested and confirmed.

An examination of the last five rows of values in Table XXIX shows that for gaseous water and hydrochloric acid, produced out of the gaseous elements, the ratio of free to total energy is not far from unity, but that it has widely divergent values in the case of the other gaseous substances, indicating the absence of any simple relations.

The author wishes here to express his very sincere thanks to

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[1] This will be more obvious from the following summary of the free energies per equivalent of salt:

	Cl.	Diff.	Br.	Diff.	I.	Diff.
Hg(ous)	24700		21400		13400	
		900		1600		2500
Ag	25600		23000		15900	
		2500		700		900
Cu(ous)	28100		23700		16600	

Prof. A. A. Noyes for the valuable advice received while carrying out this work. Without this advice it would not have arrived at its present state.

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ON THE APPLICABILITY OF RAOULT'S LAWS TO MOLECULAR WEIGHT DETERMINATIONS IN MIXED SOLVENTS AND IN SIMPLE SOLVENTS WHOSE VAPOR DISSOCIATES.

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BECKMANN[1] has recently determined the molecular weights of several substances in concentrated sulphuric acid by the boiling-point method. Now the researches of Deville and Troost have shown that the vapor of sulphuric acid is completely dissociated into water and sulphur trioxide, and the question arises as to whether it is justifiable to apply to a case of this kind the simple laws of Raoult for the lowering of the vapor-pressure and the raising of the boiling-point.

The solvent used by Beckmann is described as follows: "Zu allen Versuchen wurde die verwendete reine Schwefelsäure aus einer Glasretorte fraktioniert destilliert. Nur der konstant bei 331.7° (unkorrigiert) übergehende mittlere Teil fand Verwendung." This sulphuric acid of constant boiling-point contains about 1.5 per cent. of water and must therefore be regarded, not as a simple liquid, but as a binary mixture. If instead of regarding it as a mixture of sulphuric acid and water we regard it as a mixture of sulphur trioxide and water, it is obvious that it does not differ essentially from any other binary mixture (such as a 20 per cent. hydrochloric acid solution for example) which has a constant boiling-point.

The following thermodynamic considerations lead to the interesting conclusion that, while pure sulphuric acid cannot be used for molecular weight determinations, the use of the constant boiling acid employed by Beckmann is entirely justifiable. In-

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[1] Z. physik. Chem. 53, 129 (1905).