[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF BROMINE COMPOUNDS.

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Taking as the standard state of bromine the one which is stable at 25° and a pressure of one atmosphere, namely liquid bromine, we are in a position to calculate the free energy of the various known forms of elementary bromine, of bromide and polybromide ions, and of all the known compounds of bromine with oxygen and hydrogen.

Elementary Bromine.

$2Br(l) = Br_2(g)$.—The vapor pressure of liquid bromine has been determined by Roozeboom[1] and by Ramsay and Young.[2] Both sets of measurements show excellent self-consistency when tested by plotting $\log p$ against $1/T$. In both cases a few scattering points are obviously in error, but the remaining points give for each set a straight line, and these two straight lines are not only near to one another but are parallel, that is, they have the same slope. From this slope we may determine directly the heat of vaporization at the average temperature (32°) of the points which were plotted. We thus find $\Delta H_{305} = 7530$. The heat capacity of liquid bromine has not been accurately determined but we may take as an approximate value for this reaction $\Delta\Gamma = -9.6$. Since we have adopted permanently for $Br_2(g)$ the value[3] $C_p = 6.5 + 0.004T$, this means that we are taking for $Br(l)$, $C_p = 8.05 + 0.002T$, an equation which is purely formal, introduced for convenience, and only has experimental significance inasmuch as it gives the approximate value of the specific heat of liquid bromine at room temperature. Having once assumed this equation we must of course apply it consistently in our future equations. We therefore write $\Delta H = 10450 - 9.6\,T$, which agrees almost precisely with the heat of vaporization determined by Berthelot at 60° and is a trifle higher than the value obtained by Thomsen. The final free energy equation is

$$\Delta F^\circ = 10450 + 9.6T \ln T - 87.21T, \qquad (1)$$

where the value of $I = -87.21$ is obtained from the following determination of ΔF°_{298}. The vapor pressure of bromine at 25° is 208 mm. of mercury if we use the data of Roozeboom, and 213 mm. if we use the data of Ramsay and Young. The latter measurements are in somewhat better agreement with the determinations of the boiling point of bromine, and we shall therefore accept Ramsay and Young's value. Hence,

$$\Delta F^\circ_{298} = 755 \text{ cal.} \qquad (2)$$

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[1] Roozeboom, *Rec. trav. chim.*, **3**, 73 (1884).

[2] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[3] Lewis and Randall, THIS JOURNAL, **34**, 1128 (1912).

We may use Equation 1 to find the boiling point of bromine by writing $\Delta F^\circ = 0$ and solving for T. This gives 58.7°. Such a calculation from an equation like (1) is very instructive, since it shows at once the necessity of the very highest numerical accuracy, notwithstanding the fact that such a coefficient as that of T ln T is uncertain, and that the original choice of this constant, rather than some neighboring one, is not very important. It will of course be obvious that such an equation will not be valid over a very wide temperature interval, and if it is so used it will be in a purely formal manner. It must also be noted that we have throughout assumed bromine vapor to be a perfect gas. If reliable data concerning the density and compressibility of the vapor were available we should take as the normal state of $Br_2(g)$ not the gas at one atmosphere but in the condition where its activity is x times as great as at $1/x$ atmos., where x is a large number.

$Br(l) = Br(s)$.—The heat of fusion of bromine was found by Regnault to be 1290 cal. per gram atom. The heat capacity of solid bromine has not been much studied, but judging from the measurements of Koref[1] at low temperatures it is not far from that of liquid bromine at ordinary temperatures. We may write, therefore, $\Delta\Gamma = 0$ and $\Delta H_0 = -1290$. Taking the freezing point as -7.3° where $\Delta F^\circ = 0$, we find

$$\Delta F^\circ = -1290 + 4.86T; \quad \Delta F^\circ_{298} = 157. \qquad (3)$$

Without a direct determination of either melting point or heat of fusion we could make this same calculation from the experiments of Ramsay and Young and those of Cuthbertson[2] upon the vapor pressure of solid bromine. We have plotted their data in the usual way, namely, log p against $1/T$. From the slope of the curve, which gives the heat of sublimation, and from the heat of vaporization of the liquid which we have already discussed, we find a value for the heat of fusion of 1245 cal., which, within the limits of error of the vapor-pressure measurements, coincides with the value of Regnault. Likewise from the vapor-pressure measurements we could calculate directly the value of ΔF°_{298}, and here too the calculation, although subject to large errors, agrees with the value which we have given. Similar calculations, based upon more accurate data, we have already made in discussing the various forms of elementary sulfur.[3]

$Br_2(g) = Br_2(\text{in } CCl_4, N = 1)$.—Before proceeding to determine the free energy of aqueous bromine, partly as a step in this process, but also on account of the frequent use of carbon tetrachloride as a solvent in distribution experiments, and in general where it is necessary to maintain a phase in which the activity of the solute is kept at a known constant value, it will be desirable to calculate the free energy of bromine dissolved

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[1] Koref, *Ann. Physik,* [4] **36,** 49 (1911).

[2] Cuthbertson, *Proc. Roy. Soc.,* (*A*) **85,** 306 (1911).

[3] Lewis and Randall, THIS JOURNAL, **36,** 2468 (1914).

in CCl_4. Since carbon tetrachloride as a nonpolar substance has essentially the characteristics of a normal liquid, it will be preferable to use a convention for the standard condition in this solvent differing from the one which we have employed in the case of water. We shall therefore use not the concentration of the solute but its mol fraction, N, and we shall take as a standard or normal condition[1] the one in which the activity (or vapor pressure) is 1/N times as great as that in a dilute solution in which the mol fraction of the solute is N. Mr. Storch, in this laboratory, has made a number of determinations, which will shortly be published, of the vapor pressure of bromine from dilute solutions in CCl_4. He finds at 25°, $p = 0.539$ N, where p is the partial vapor pressure of Br_2 in atmospheres and N is its mol fraction. The measurements extend from $N = 0$ to $N = 0.025$. It is evident that the solution of Br_2 in CCl_4 does not obey Raoult's law over the whole range of concentrations, for the equation would lead when $N = 1$ to a vapor pressure nearly twice that of pure liquid bromine. Our free energy equation in this case is simply

$$\Delta F^\circ_{298} = -R'T \ln (N/p) = -366. \qquad (4)$$

$2Br(e) = Br_2$ (in CCl_4, $N = 1$).—Adding Equations 2 and 4 gives

$$\Delta F^\circ_{298} = 389 \text{ cal.} \qquad (5)$$

Br_2 (in CCl_4, $N = 1$) = Br_2(aq).—In discussing the distribution of bromine between water and carbon tetrachloride we shall use the mol fraction of the bromine to express the composition of the CCl_4 phase and, as usual, mols Br_2 to 1000 g. of water to express that of the aqueous phase. The well-known experiments of Jakowkin,[2] on the distribution coefficient in this system, we have reviewed in detail and we arrive at conclusions which differ somewhat from those which have usually been drawn from these measurements. His experiments in dilute solutions are vitiated by the fact that the bromine hydrolyzes in the aqueous phase to the extent of 10% or more[3] and his figures are for the total bromine and not for that which occurs simply as Br_2. Mr. Storch in hitherto unpublished work, to which we have referred, has determined the partition of bromine between CCl_4 and water containing HCl at $0.001M$. It was assumed that water containing this small amount of hydrochloric acid, would prevent the hydrolysis of the bromine, but would not affect materially the activity of the dissolved Br_2. In order to test this assumption similar partition experiments were made between CCl_4 and water containing

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[1] The advantage of this choice is obvious in the case of two liquids which like benzene and toluene in all mixtures form perfect solutions (see Lewis, THIS JOURNAL, **30,** 668 (1908)). Here it is evident that F° is the same for C_6H_6 (l) and C_6H_6 (in toluene).

[2] Jakowkin, *Z. physik. Chem.*, **18,** 583 (1895).

[3] Bray and Connolly, THIS JOURNAL, **33,** 1485 (1911).

an equivalent amount of sulfuric acid. He found for m/N, 0.3705 with HCl and 0.3710 with H_2SO_4, where N is the mol fraction of Br_2 in the CCl_4 and m the number of mols per 1000 g. H_2O. We shall write $m/N = 0.371$. In these measurements N was equal to 0.01373. When we consider Jakowkin's experiments at the higher concentrations, where hydrolysis plays no important role, we find that this partition coefficient, owing to the high concentrations, varies more than the ratio which we use involving the mol fraction instead of the concentration. Without repeating the rather laborious calculations which we have made in reducing his measurements to our units (assuming that Br(l) and CCl_4 mix without change of volume) we may state merely that the value of m/N varies regularly from 0.35 at $N = 0.14$ to values in dilute solutions which agree closely with the one obtained by Storch, 0.371. Taking this value as the partition ratio in dilute solution we find for this reaction

$$\Delta F^\circ_{298} = -R'T \ln(m/N) = 588. \qquad (6)$$

$2Br(l) = Br_2(aq)$.—Adding Equations 5 and 6 we find

$$\Delta F^\circ_{298} = 977. \qquad (7)$$

Such an equation as (7) is of course applicable only to solutions which are so dilute that the activity of the solute is proportional to the concentration. It is interesting to see the magnitude of the deviation from such proportionality in the case of a saturated aqueous solution of bromine by comparing the measured solubility of bromine with that obtained from Equation 7. Bray and Connolly[1] found for the saturated solution of bromine at 25°, $m = 0.2068$, whereas from Equation 7, writing $977 = -R'T \ln m$; $m = 0.1923$, a difference of 7.5%.

$Br_2(g) = 2Br(g)$.—The dissociation of bromine vapor into the monatomic gas has been studied by Perman and Atkinson[2] who measured the density of bromine vapor between 650° and 1050°. Their method of calculation is not easy to follow, but if we divide what they call vapor density by 80.3, which seems to be the best value of this quantity at the lowest temperature (where we may assume that no dissociation occurs) we should get the ratio between the actual density and the density calculated on the assumption of no dissociation. The equilibrium constants, K_p, calculated from these ratios, are given in the second row of Table I, the absolute temperature being given in the first row.

TABLE I.

T	1073	1123	1173	1223	1273	1323
K_p	0.000179	0.000403	0.00140	0.00328	0.0077	0.0182

Now if we plot log K_p against $1/T$ we find that at the four highest temperatures, which are the only ones at which the dissociation is considera-

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[1] Bray and Connolly, THIS JOURNAL, **33**, 1485 (1911).

[2] Perman and Atkinson, *Z. physik. Chem.*, **33**, 215, 577 (1900).

ble, the points lie on a straight line and the slope of this line multiplied by 4.579 gives at the average temperature of the measurements $\Delta H_{1250} = 53700$. Assuming that Br has the same heat capacity as other monatomic gases, $\Delta\Gamma = 3.5 - 0.004T$, whence $\Delta H_0 = 52400$, and

$$\Delta F^\circ = 52400 - 3.5T \ln T + 0.002T^2 - 9.07T \quad (8)$$

where the value of $I = -9.07$ was obtained from $\log K_{1250} = -2.27$ as read from the plot. Since the calculation of ΔH from the density measurements is greatly affected by small errors, the value of ΔF°_{298} may easily be in error by several thousand calories. We have

$$\Delta F^\circ_{298} = 43900. \quad (9)$$

$Br(l) = Br(g)$.—Combining Equations 1 and 2, respectively, with 8 and 9, $\Delta F^\circ = 31425 + 3.05T \ln T + 0.001T^2 - 48.14T$;

$$\Delta F^\circ_{298} = 22328. \quad (10)$$

Hydrobromic Acid; Bromide Ion; Tribromide Ion; Pentabromide Ion.

$^1/_2H_2 + {}^1/_2Br_2(g) = HBr(g)$.—The dissociation of gaseous hydrogen bromide has been investigated by von Falckenstein[1] at the temperatures 1024°, 1108° and 1222°. His measurements lead directly to the corresponding three values of $\log K_p$, 2.60, 2.44 and 2.27.

In order to calculate from these measurements the free energy of this reaction at other temperatures we must know the thermal quantities involved. The heat capacities of the three gases are given in our former paper[2] and thence we find $\Delta\Gamma = -0.00145T$. The heat of the reaction at room temperatures calculated from the measurements of Thomsen is 11900, and from those of Berthelot 12300, average 12100, and $\Delta H_0 = -12000$. The complete free energy equation is therefore

$$\Delta F^\circ = -12000 + 0.000725T^2 - 3.5T, \quad (11)$$

where the value of I, −3.5, is the mean of the values obtained at von Falckenstein's three temperatures, namely, −3.57, −3.46, and −3.43. Hence

$$^1/_2H_2 + {}^1/_2Br_2(g) = HBr(g);\ \Delta F^\circ_{298} = -12970. \quad (12)$$

While the extrapolation to 25° from von Falckenstein's experiments is made over a wide temperature range, the probable errors in the specific heats and in the heat of reaction are not sufficient to produce an uncertainty of more than 100 to 150 cal. in the value of ΔF°_{298}. This calculation therefore is probably at least as reliable as one which we shall now make and which is based upon the measurements by Bodenstein and Geiger[2] of the e. m. f. of the hydrogen, bromine, hydrobromic acid cell. They used two half cells both containing the same concentrated aqueous

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[1] von Falckenstein, *Z. physik. Chem.*, **68**, 270 (1909).

[2] Lewis and Randall, THIS JOURNAL, **34**, 1128 (1912).

[3] Bodenstein and Geiger, *Z. physik. Chem.*, **49**, 70 (1904).

hydrobromic acid. In one was a hydrogen electrode, in the other a bromine electrode, enough bromine being added to the hydrobromic acid so that the vapor pressures of the bromine and hydrobromic acid could be simultaneously determined. Knowing then the vapor pressure of Br_2, HBr and H_2, the electromotive force should be represented by the equation

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}} \ln \frac{[HBr]}{[H_2]^{1/2}[Br_2]^{1/2}}.$$

The three cells in which Bodenstein and Geiger measured the electromotive forces and vapor pressures give for **E**° the values 0.557, 0.558 and 0.549 v. at 30°. The differences between these values of **E**° may be partly due to experimental error, but they must in part be due to the error in assuming the hydrobromic acid to be the same in the two halves of the cell, even though enough bromine is added on one side to change appreciably the vapor pressure of HBr, as shown by the authors themselves. The mean of their values gives $\Delta F^\circ_{303} = -12760$, or making the slight correction to 25° C., $\Delta F^\circ_{298} = -12740$. Their value therefore agrees as well as could be expected with the one which we have given above. We shall accept the values obtained in Equations 11 and 12.

Before leaving Equation 11 it may be worth while to make a comment, which, though obvious when stated, has not to our knowledge previously been made. Ordinarily it has been assumed that in a reaction like the dissociation of HBr the degree of dissociation would, except for a possible change in the sign of the heat of reaction, increase with the temperature, and that at very high temperatures the dissociation would be complete. This is by no means the case. We have hitherto considered three reactions, namely, the dissociation of NO, of HI and of HBr, in which neither the number of molecules nor the number of atoms within a molecule changes. In such cases, as was first pointed out by Haber, not only is $\Delta\Gamma$ small and the heat of reaction nearly constant, but the value of I is small and the free energy equation approximates closely to the simplest form $\Delta F^\circ = \Delta H_0$. In such a case it is evident, since $-R'T \ln K = \Delta F^\circ$ = constant, that as the temperature is indefinitely increased ln K must approach zero, and therefore K must approach unity. In other words, the degree of dissociation will approach 50% and not 100% as the temperature is increased. In the actual cases which we have considered there are additional small terms in the free energy equation, but nevertheless it is evident that in any temperature range in which Equation 11 is approximately valid the degree of dissociation of HBr cannot exceed 50%, except of course inasfar as other reactions enter, such as the dissociation of H_2 and Br_2 into their monoatomic forms.

$^1/_2H_2$ + Br(*l*) = HBr(g).—Combining Equations 1 and 2, respectively, with Equations 11 and 12, we find

$$\Delta F^\circ = -6775 + 4.8T \ln T + 0.000725T^2 - 47.10T;\ \Delta F^\circ_{298} = -12592. \qquad (13)$$

$Br(l) + \ominus = Br^-$.—The free energy of formation and of dilution of aqueous hydrobromic acid have been exhaustively investigated by Lewis and Storch in the paper to which we have already referred and which will shortly be published. As the final result of this investigation, against the standard hydrogen electrode, at 25°, the potential of liquid bromine in the presence of bromide ion at (hypothetical) molal concentration is —1.0659 v., a value which is accurate to within a few tenths of a millivolt. Hence for the above reaction

$$\Delta F^\circ_{298} = -n\mathbf{E}^\circ\mathbf{F}' = \mathbf{E}^\circ\mathbf{F}';\ \text{or}\ \Delta F^\circ_{298} = -24594. \qquad (14)$$

$Br^- + Br_2(aq) = Br_3^-$.—The equilibrium in the formation of tribromide was studied by Jakowkin[1] who determined the partition of bromine between carbon tetrachloride and aqueous solutions of KBr at 25°. Assuming that KBr_3 and KBr are in dilute solution ionized to the same extent at the same concentration, the ratio of KBr_3 to KBr should be approximately constant. In fact a complete recalculation of Jakowkin's data gives a much better constant than he himself obtained. In this calculation we have used the partition coefficient given above, after recalculating his concentrations in CCl_4 to mol fractions. The results of Jakowkin, as recalculated, are given in Table II. We have used only his measurements with dilute KBr and dilute Br_2. The first column gives the concentration of Br_2 as such in the aqueous phase, the second the concentration of KBr used, and the third column the values of the constant $K = (Br_3^-)/[(Br^-)(Br_2)]$.

TABLE II.

Br_2.	KBr.	K.
0.00198	0.0625	16.50
0.00377	0.0625	16.15
0.00710	0.0625	16.07
0.00986	0.0625	16.04
0.00145	0.1250	16.32
0.00345	0.1250	16.35
0.00610	0.1250	16.20
0.00880	0.1250	16.05

Dr. Linhart in this laboratory has made calculations based upon Worley's measurements[2] in more concentrated solutions and has shown that, when due allowance is made for the formation of pentabromide, Worley's measurements lead to the same constant as Jakowkin's. Moreover, Jakowkin's measurements are corroborated by the similar investigation of Storch with solutions of HBr. Taking K = 16.2 we find

$$\Delta F^\circ_{298} = -1650. \qquad (15)$$

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

[2] Worley, *J. Chem. Soc.*, **87,** 1118 (1905).

$3Br(l) + \ominus = Br_3^-$.—Adding Equations 7, 14 and 15, we find

$$\Delta F^\circ_{298} = -25267. \qquad (16)$$

$Br_3^- + Br_2(aq) = Br_5^-$.—There can hardly be any doubt that not only tribromide but higher polybromides exist in solution. Nevertheless, since a substance like KBr_5 is formed in appreciable amounts only when the concentration of bromine is high, and therefore the laws of the dilute solution are not necessarily valid, the calculation of such a constant as $(Br_5^-)/(Br_2)(Br_3^-)$ is attended with considerable uncertainty. The calculations made by Linhart from the experiments of Worley show very fair constancy in K, which he takes as 1.2, whence we may obtain as an approximate value

$$\Delta F^\circ_{298} = -110. \qquad (17)$$

$5Br(l) + \ominus = Br_5^-$.—Adding Equations 7, 16 and 17,

$$\Delta F^\circ_{298} = -24400. \qquad (18)$$

$Br_2(aq) + H_2O(l) = H^+ + Br^- + HBrO(aq)$.—From careful measurements of the conductivity, Bray and Connolly[1] have determined the degree of hydrolysis of bromine solutions and found

$$K_{298} = (H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}.$$

Hence

$$\Delta F^\circ_{298} = 11310. \qquad (19)$$

$Br(l) \oplus {}^1/_2H_2 + {}^1/_2O_2 = HBrO(aq)$.—Owing to our lack of knowledge of the dissociation constant of hypobromous acid it is impossible to determine the free energy of hypobromite ion. We must therefore at present be content with the determination of that of the free acid. Combining Equations 7, 14 and 19 with Equations 9 and 54 of our paper[2] on the free energy of oxygen and hydrogen compounds, we find

$$\Delta F^\circ_{298} = -19739. \qquad (20)$$

$Br(l) + 3H_2O(l) + 5\oplus = 6H^+ + BrO_3^-$.—Sammet[3] measured the potential at 25° of a platinum electrode dipping into an aqueous solution of bromic acid saturated with liquid bromine. He used solutions of $HBrO_3$ ranging from 0.001 *M* to 1.0 *M*. At present only the results in dilute solutions can be used for exact calculations. Thus the potential in the case of the 0.001 *M* $HBrO_3$ against the normal calomel electrode was —0.929 v. By the use of the Planck formula he calculated the liquid potential to be 0.031 v. which is probably as nearly correct as the measurements themselves. The potential therefore against the normal calomel electrode, excluding liquid potentials, is —0.960 v., or against the hydrogen electrode is —1.238 v. We have then the equation —1.238 =

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[1] Bray and Connolly, THIS JOURNAL, **33**, 1485 (1911).

[2] Lewis and Randall, *Ibid.*, **36**, 1969 (1914).

[3] Sammet, *Z. physik. Chem.*, **53**, 678 (1905).

$E^\circ - RT/5F \ln (H^+)^6(BrO_3^-)$. Taking the degree of dissociation of 0.001 *M* $HBrO_3$ as 0.97,

$$E^\circ = -1.487;\ \Delta F^\circ_{298} = 171550. \qquad (21)$$

$Br(l) + {}^3/_2O_2 + \ominus = BrO_3^-$.—Combining Equation 21 with Equations 9 and 54 of our paper on oxygen and hydrogen compounds, we find

$$\Delta F^\circ_{298} = 1690. \qquad (22)$$

Summary.

The following table gives the free energy of formation of the several forms of elementary bromine and of the bromine compounds which have been considered in this paper:

Substance.	ΔF°_{298}.	Equation.	Substance.	ΔF°_{298}.	Equation.
$Br(l)$	0	..	$HBr(g)$	—12592	13
$Br_2(g)$	755	1, 2	Br^-	—24594	14
$Br(s)$	157	3	Br_3^-	—25267	16
Br_2 (in CCl_4, N = 1)	389	5	Br_5^-	—24400	18
$Br_2(aq)$	977	7	$HBrO(aq)$	—19739	20
$Br(g)$	[22328]	10	BrO_3^-	1690	22

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE MERCURY ELECTRODE AGAINST MERCUROUS ION.

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One of the lines of work in progress in this laboratory is the accurate measurement of the electrode potentials of the chemical elements. The present paper deals with the determination of the electrode potential of mercury against Hg_2^{++}.

Ogg[1] has shown, in a qualitative way, that the mercurous ion in a water solution of a mercurous salt, is chiefly in the form of Hg_2^{++}, and to some extent also in the form of Hg^+. But for obvious reasons (notably hydrolysis and oxidation) mercurous nitrate is not a suitable substance for accurate electrochemical measurements. Therefore, for the present investigation, mercurous perchlorate was chosen, because it was shown by Ley[2] that the extent to which this salt hydrolyzes is extremely small, and that the small amount of hydrolysis products thus formed are soluble in water. An almost neutral solution of this salt can be prepared, not by reducing the mercuric salt in solution by means of metallic mercury, but by treating pure mercurous oxide with a water solution of pure perchloric acid. The details of preparation, as well as the method of measurements, are given in the experimental part of this paper. In the

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[1] Ogg, *Z. physik. Chem.*, **27**, 295 (1898).

[2] Ley, *Z. Electrochem.*, **10**, 302 (1904).