

On the Complexity of Cadmium and Silver Sulphate

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A. SOME CHARACTERISTICS OF AQUEOUS SOLUTIONS OF 2-2-SULPHATES

In some recent papers aqueous solutions of sulphates of divalent metals have been studied. *E.g.* Fronaeus^{1,2} and Näsänen³ studied copper sulphate and Leden⁴ cadmium sulphate. If the results of the measurements should be accounted for by assuming formation of complexes in the solutions, it turned up that it was necessary to presume polynuclear complexes to be formed. The complex systems thus appeared so intricate that they could not be completely unravelled. On the other hand it seems rather astonishing that the sulphate systems should be so complicated, as measurements on solutions of different 2-2-sulphates seem to indicate that the individual differences between them are rather small, and thus it seems natural to suppose that the conditions should be rather simple in all the solutions. Some examples of this remarkable uniformity are pointed out in the following.

The depression of the freezing points at increasing concentration of 2-2-sulphates is described by very similar functions for all these sulphates, as can be seen from the tables of Landolt-Börnstein, from which some values are interpolated in Table 1. Even at higher concentrations than those of the table the curves coincide remarkably well.

Table 1. Depression of the freezing point in some solutions of 2-2-sulphates.

Conc. <i>M</i>	Molal depression of the freezing point degree M^{-1}						
	$CdSO_4$	$CoSO_4$	$CuSO_4$	$FeSO_4$	$MgSO_4$	$NiSO_4$	$ZnSO_4$
0.02	2.57		2.50	2.57	2.62	2.57	2.58
0.1	2.22	2.19	2.13	2.22	2.26		2.28
0.2	2.03		1.93	2.01	2.07		2.08

*Table 2. Osmotic coefficients according to Plake⁵ in 0.3 *M* solutions of some 2-2-sulphates*

	$CdSO_4$	$CuSO_4$	$MgSO_4$	$MnSO_4$	$NiSO_4$	$ZnSO_4$
OC_f :	0.53	0.48	0.54	0.55	—	0.54
OC_b :	0.41	0.44	0.47	0.42	0.43	0.44

Similarly Plake⁵ has made a comparison of osmotic coefficients (OC), obtained from measurements of the elevation of the boiling point (OC_b) and the depression of the freezing point (OC_f), from which it is seen that the differences between solutions of varying 2-2-sulphates are surprisingly small. (See Table 2.)

Finally Güntelberg⁶ has drawn the mean activity coefficients of $CdSO_4$, $MgSO_4$, $NiSO_4$, and $ZnSO_4$ as functions of the concentration and has obtained adjacent curves with much smaller individual variations than for solutions of representative 1-1-electrolytes. Also Hass and Jellineck⁷ point out that the mean activity of $CdSO_4$ does not detach from sulphates such as $CaSO_4$ or $MgSO_4$ unlike other cadmium salts, *e.g.* the chloride, whose mean activity decreases much faster than the chlorides of calcium or magnesium at increasing concentrations.

In the following an attempt has been made to investigate the cadmium-sulphate system by determining the concentrations of free sulphate ions in it. This has been done by a new method, described in part C of the present paper. By using this method the complex formation between silver and sulphate ions must be known in the same ionic environment (3 C $NaClO_4$).

B. POTENTIOMETRIC MEASUREMENTS WITH SILVER ELECTRODES IN SOLUTIONS CONTAINING SILVER AND SULPHATE IONS IN A MEDIUM WITH A HIGH IONIC STRENGTH

The measurements were performed according to methods previously described^{8,9}, *i.e.* as potentiometric titrations with a silver-silver chloride electrode according to Brown¹⁰. The temperature of the thermostat was 25.16° C. The potentiometer was from N. C. Jensen, Copenhagen, type 10 A and the "multiflex" galvanometer type MG 2 from H. Tillquist, Stockholm, with a sensitivity of $2 \cdot 10^{-8}$ A/mm.

Stock solutions of silver and sodium perchlorate were prepared as previously described⁹. No foreign ions could be proved in the used sodium sulphate, *p.a.* The sulphate concentrations of the stock solutions were determined by precipitating with barium chloride.

As a reference electrode mercury in 3 C sodium perchlorate saturated with mercury (I) sulphate was used. The emfs measured were practically always reproducible within 0.1 mV.

Sodium perchlorate has been added to obtain as constant activity conditions as possible. It is doubtful, however, whether the solutions should be made so, that the ionic strength

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (1)$$

becomes constant, or if it is better to choose the ionic environment so, as to maintain the sodium ion concentration at a constant value. Therefore both the kinds of measure series have been performed. By comparing the two kinds of series it is also possible to find out how a change of the ionic strength affects the potential of the silver electrode (see below). By this comparison it must be kept in mind that the liquid junction potentials are different in the two cases. If this potential is calculated according to Henderson as is

previously described ⁹, it is found to be insignificant in the series with a constant ionic strength = 3 C. On the other hand a correction has been introduced for this potential in the series, where the sodium ion concentration is constant = 3 C (Table 4), where the emf E is given as the sum of two terms, the first of which being the emf directly measured and the second one thus being the correction for the diffusion potential. The notations in the tables and in the equations are the same as have previously ^{8,9} been used (see also (5), (6), and (7) in the present paper).

As long as $[\text{SO}_4^{2-}] < 0.6$ C all the values of $F_1(\text{SO}_4^{2-})$, obtained in Table 3, from the equation

$$F_1(\text{SO}_4^{2-}) = \frac{c_{\text{Ag}} - [\text{Ag}^+]}{[\text{Ag}][\text{SO}_4^{2-}]} \quad (2)$$

satisfy the equation of the straight line

$$F_1(\text{SO}_4^{2-}) = 1.7 + 1.9 [\text{SO}_4^{2-}] \quad (3)$$

which means that the potentiometric measurements may be accounted for by assuming the complexes AgSO_4^- and $\text{Ag}(\text{SO}_4)_2^{3-}$ to have been built up in the solutions. Their complexity constants are $\beta_1 = (1.7 \pm 0.05) \text{ C}^{-1}$ and $\beta_2 = (1.9 \pm 0.1) \text{ C}^{-2}$. No polynuclear complexes exist in the solutions, as $F_1(\text{SO}_4^{2-})$ is independent of c_{Ag} . For the theory, *vide ref.* 8.

The complex formation function or ligand number ⁴ \bar{n} of the silver sulphate system is

$$\bar{n} = \frac{1.7[\text{SO}_4^{2-}] + 3.8[\text{SO}_4^{2-}]^2}{1 + 1.7[\text{SO}_4^{2-}] + 1.9[\text{SO}_4^{2-}]^2} \quad (4)$$

valid at a constant ionic strength of 3 C (NaClO_4). The function $\bar{n}/[\text{SO}_4^{2-}]$ will be used later on by the following study of the cadmium sulphate-system.

In Table 4 the corresponding measurements and calculations at a constant sodium ion concentration of 3 C are collected. $F_1(\text{SO}_4^{2-})$ is still represented by a straight line, from which the complexity constants $\beta_1 = (1.7 \pm 0.05) \text{ C}^{-1}$ and $\beta_2 = (1.0 \pm 0.1) \text{ C}^{-2}$ result.

In the solutions in Table 4 the ionic strength I , calculated from (1), increases for increasing sulphate concentrations, and thus can be conveniently written as $I = (3 + \Delta I)$ C. ΔI is given in mC in Table 4. By comparing the emfs E of the Tables 3 and 4 it is possible to calculate how much a quantitative change of the ionic strength, other circumstances unaltered, influences the potential of the silver electrode. In these tables E is a measure of the decrease of this potential, as the potential of the silver electrode decreases at increasing sulphate concentrations. The difference ΔE between the silver potentials at $I = 3$ C and $[\text{Na}^+] = 3$ C at the same sulphate concentrations is to be found

Table 3. Titrations with 1 C sodium sulphate on solutions of silver perchlorate containing sodium perchlorate to an ionic strength of 3 C.

c_{Ag} mC	c_{SO_4} mC	E mV	$[\text{Ag}^+]$ mC	$[\text{SO}_4^{2-}]$ mC */	$F_1(\text{SO}_4^{2-})$ C ⁻¹ (2)
3.33	0	0	3.33	0	
3.25	24.4	1.7	3.12	24.3	1.71
3.17	47.6	3.4	2.90	47.3	1.97
3.10	69.8	5.0	2.74	69.4	1.90
3.03	90.9	6.5	2.59	90.4	1.88
2.90	130.5	9.4	2.31	130	1.97
2.78	167	12.1	2.08	166	2.03
2.67	200	14.6	1.89	199	2.08
2.47	259	19.1	1.59	258	2.15
2.22	333	24.9	1.266	332	2.28
1.905	428	32.8	0.930	427	2.46
1.667	500	39.2	0.726	499	2.60
1.333	600	48.8	0.500	599	2.78
1.111	667	56.2	0.375	666	(2.95)
0.832	750	66.9	0.247	749	(3.16)
10.00	0	0	10	0	
9.76	24.4	1.7	9.36	24	1.56
9.52	47.6	3.4	8.69	46.8	2.04
9.30	69.8	5.1	8.20	68.7	1.95
9.09	90.9	6.6	7.74	89.5	1.95
8.69	130.5	9.4	6.94	129	1.96
8.33	167	12.1	6.25	165	2.02
8.00	200	14.6	5.67	198	2.08
7.41	259	19.1	4.76	256	2.18
6.67	333	24.8	3.81	330	2.27
5.71	428	32.7	2.81	425	2.43
5.00	500	39.1	2.19	497	2.58
4.44	556	44.3	1.79	553	2.68
4.00	600	48.9	1.49	597	2.82
33.3	0	0	33.3	0	
32.5	24.4	1.5	31.4	23.3	1.50
31.7	47.6	3.1	29.5	45.4	1.64
31.0	69.8	4.6	27.7	66.5	1.79
30.3	90.9	6.3	26.1	86.7	1.86
29.0	130.5	9.1	23.4	125	1.91
27.8	167	11.7	21.1	160	1.99
26.7	200	14.1	19.3	193	1.99
25.6	231	16.5	17.5	223	2.08

Table 3 contin.

c_{Ag} mC	c_{SO_4} mC	E mV	$[Ag^+]$ mC	$[SO_4^{2-}]$ mC */	$F_1(SO_4^{2-})$ C^{-1} (2)
24.7	259	18.7	16.1	250	2.14
22.2	333	24.7	12.7	323	2.32
19.05	428	32.5	9.40	418	2.46
16.7	500	38.9	7.33	490	2.73
14.8	556	44.3	5.96	547	2.70
13.3	600	48.9	4.98	592	2.82
100.0	0	0	100	0	
97.6	24.4	1.4	94.7	21.5	1.43
95.2	47.6	3.0	89.0	41.4	1.69
93.0	69.8	4.7	83.3	60.1	1.94
90.9	90.9	6.2	78.6	78.6	1.99

* $[SO_4^{2-}]$ has been computed from the equation $[SO_4^{2-}] = c_{SO_4} - \nu(c_{Ag} - [Ag^+])$, where $\nu = \frac{\beta_1 + 2\beta_2[SO_4^{2-}]}{\beta_1 + \beta_2[SO_4^{2-}]}$, i.e. $1 < \nu < 2$. Cf. 4, p. 16, and 8, p. 1321.

Table 4. Titrations with a solution containing 1 C sodium sulphate and 1 C sodium perchlorate on a solution containing 10 mC silver perchlorate and 2.99 C sodium perchlorate. Ionic strength 3 C + Δ I C.

c_{Ag} mC	c_{SO_4} mC	E mV	$[Ag^+]$ mC	$[SO_4^{2-}]$ mC */	$F_1(SO_4^{2-})$ C^{-1} (2)	ΔE mV	ΔI mC	$\frac{\Delta E}{\Delta I}$ mV/C
10.00	0	0	10.00	0			0	
9.76	24.4	1.6 + 0.0	9.40	24.0	1.60	0.1	20	(5.0)
9.52	47.6	3.2 + 0.1	8.79	46.9	1.77	0.1	50	(2.0)
9.30	69.8	4.7 + 0.1	8.30	68.8	1.75	0.3	70	4.3
9.09	90.9	6.1 + 0.2	7.83	89.6	1.80	0.3	90	3.3
8.69	130.5	8.7 + 0.2	7.07	129	1.78	0.5	130	3.8
8.33	167	11.2 + 0.3	6.39	165	1.96	0.6	170	3.5
8.00	200	13.5 + 0.3	5.85	198	1.86	0.8	200	4.0
7.41	259	17.6 + 0.4	4.96	256	1.93	1.1	260	4.2
6.67	333	22.9 + 0.6	4.01	330	2.01	1.3	330	3.9
5.71	428	30.1 + 0.7	3.02	425	2.10	1.9	430	4.4
5.00	500	35.8 + 0.8	2.43	497	2.21	2.5	500	5.0
4.00	600	44.7 + 0.9	1.70	597	2.26	3.3	600	(5.5)

* Cf. note under Table 3.

Mean: 4

in Table 4. This difference seems to be about proportional to the increase ΔI of the ionic strength, as is seen from the rather constant values of $\frac{\Delta E}{\Delta I}$ in the last column of Table 4. As a mean of the increasing potential of the silver electrode at increasing ionic strength the value 4 mV/C is obtained. This value is to be used for some measurements with silver electrodes in the cadmium sulphate system, where the ionic strength could not be maintained quite constant.

C. THE USE OF A KNOWN COMPLEX STEP SYSTEM TO DETERMINE THE CONCENTRATION OF THE FREE LIGAND

If a metal ion M can form mononuclear complexes with a ligand A, it is valid that

$$c_M = [M] + [MA] + [MA_2] + \dots + [MA_N] = [M] + \beta_1[M][A] + \beta_2[M][A]^2 + \dots + \beta_N[M][A]^N \quad (5)$$

and thus ^{cf. 8}

$$\frac{c_M}{[M]} = F(A) = 1 + \beta_1[A] + \beta_2[A]^2 + \dots + \beta_N[A]^N \quad (6)$$

where $F(A)$ is a known function of $[A]$ in a system with known complexity constants, *e.g.* the silver-sulphate system. In a solution, containing M and A, in which c_M is known but not $[A]$, the latter concentration can be computed by measuring $[M]$, *e.g.* by potentiometric methods. For this purpose it is only necessary to draw $F(A)$ in a diagram. From the measured $[M]$ the ordinate $\frac{c_M}{[M]} = F(A)$ is calculated and the corresponding abscissa $[A]$ is then directly read in the diagram, drawn beforehand. If $[M]$ has been determined with the aid of potentiometric measurements in a series of solutions with constant c_M , it may be simpler to draw E instead of $F(A)$ in the diagram, as E , too, is a function of $[A]$ only,

$$E = \frac{RT}{mF} \ln \frac{c_M}{[M]} \quad (7)$$

and thus can be used in the same manner as $F(A)$ to obtain $[A]$ from the diagram.

As for the measurements with silver electrodes in solutions containing cadmium and a small amount of silver, it was only necessary to calculate how much sulphate that has been bound by the cadmium ions. In principle the measurements have thus been carried out in such a way that the potential of a silver electrode has been measured first in a series of solutions with known

sulphate concentrations, as is already described in Table 3, and then in the same solutions containing an amount of cadmium ions, constant in the whole series. Self-evidently both the series of solutions also contain small amounts of silver ions. At increasing sulphate ion concentrations the electrode potential decreases, in the first series, without cadmium, by E_0 and in the second one by E . The difference between E_0 and E is due to the cadmium ions having bound sulphate ions, so that the silver electrode becomes a little more noble in the solutions containing cadmium ($E_0 > E$). The decrease of the concentration of free sulphate ions according to the formation of cadmium sulphate complexes is called $\Delta[\text{SO}_4^{2-}]$. Thus $F(\text{SO}_4^{2-})$, e.g. $c_{\text{Ag}}/[\text{Ag}^+]$, is changed correspondingly, causing a change in the silver electrode potential. The measured potential change is corrected, to ΔE_{corr} , for the decrease of ionic strength, that is due to the complex formation between cadmium and silver ions. Thus it is valid

$$E_0 - E + \text{corr} = \Delta E_{\text{corr}} = \frac{RT}{F} \ln \frac{[\text{Ag}^+]}{[\text{Ag}^+]_0} \quad (8)$$

The index $_0$ denotes quantities in solutions free from cadmium, whereas quantities not indicated are used for the solutions containing cadmium. As the solutions are made so, that $c_{\text{Ag}_0} = c_{\text{Ag}}$, we have

$$\begin{aligned} \Delta E_{\text{corr}} &= \frac{RT}{F} \ln \left(\frac{c_{\text{Ag}_0}}{[\text{Ag}^+]_0} : \frac{c_{\text{Ag}}}{[\text{Ag}^+]} \right) = \frac{RT}{F} \ln [\text{F}_0(\text{SO}_4^{2-}) : \text{F}(\text{SO}_4^{2-})] \\ \therefore \Delta E_{\text{corr}} &= \frac{RT}{F} \Delta \ln F(\text{SO}_4^{2-}) \end{aligned} \quad (9)$$

If ΔE_{corr} is sufficiently small, (9) can be written with good approximation

$$\Delta E_{\text{corr}} \simeq \frac{RT}{F} \cdot \frac{\Delta F(\text{SO}_4^{2-})}{F(\text{SO}_4^{2-})} \quad (10)$$

$$\text{But } \bar{n} = \frac{\sum_{n=1}^N n\beta_n[\text{SO}_4^{2-}]}{F(\text{SO}_4^{2-})} = \frac{[\text{SO}_4^{2-}] \cdot \frac{d[F(\text{SO}_4^{2-})]}{d[\text{SO}_4^{2-}]}}{F(\text{SO}_4^{2-})} \quad (11)$$

Thus (10) may be approximated to

$$\Delta E_{\text{corr}} \simeq \frac{RT}{F} \cdot \frac{\bar{n}}{[\text{SO}_4^{2-}]} \cdot \Delta[\text{SO}_4^{2-}] \quad (12)$$

$$\therefore \Delta[\text{SO}_4^{2-}] \simeq \frac{[\text{SO}_4^{2-}]}{\bar{n}} \cdot \frac{\Delta E_{\text{corr}}}{25.7} \quad (13)$$

where the numerical factor is valid at the temperature of the experiments, if ΔE_{corr} is inserted in mV. The practically usable range of (13), which is a variant of the well-known generalization of Bodländer's expression*, depends on the variation of the function $\frac{[\text{SO}_4^{2-}]}{\bar{n}}$. In our case this function passes a flat minimum at the actual range of concentration, so that (13) becomes sufficiently accurate. Random errors by measuring ΔE_{corr} will everywhere be predominant to the errors that are due to the approximations at deducing (13). $\Delta[\text{SO}_4^{2-}]$ has thus been computed by drawing the function

$$\frac{[\text{SO}_4^{2-}]}{\bar{n}} = \frac{1 + 1.7[\text{SO}_4^{2-}] + 1.9[\text{SO}_4^{2-}]^2}{1.7 + 3.8[\text{SO}_4^{2-}]} \quad (14)$$

in a large scale diagram, where the value of $[\text{SO}_4^{2-}]/\bar{n}$ is read for the known value of $[\text{SO}_4^{2-}]_0$, in the solution free from cadmium. This value together with ΔE_{corr} is inserted in (13) and $\Delta[\text{SO}_4^{2-}]$ is obtained, *i.e.* the sulphate amount that has been bound as ligands by the cadmium ions present in the corresponding solution containing a known concentration of cadmium.

D. POTENTIOMETRIC MEASUREMENTS WITH CADMIUM AMALGAM

As for the methods of measuring with cadmium amalgam electrodes, *vide* 4. Four series were performed with constant cadmium concentrations (3.33, 10, 33.3 and 100 mC) and sulphate concentrations ranging from 10 to 500 mC. Sodium perchlorate was added to a constant ionic strength = 3 C, disregarding the decrease of the ionic strength according to the complex formation. The results are summarized in Table 5, where analogously to the measurements with silver electrodes (Tables 3 and 4) E means the difference between the potential of the cadmium amalgam electrode in the solutions free from sulphate to be found at the top of Table 5 and the same potential in solutions containing sulphate. As is seen from the table, E is only slightly changed at the various values of c_{Cd} . If only mononuclear complexes should exist in the system, E would be a function of the free sulphate ion concentrations only, and as a considerable part of the sulphate is consumed in the complexes at the higher concentrations of cadmium, so that solutions with the same total concentration c_{SO_4} obtain very different concentrations, $[\text{SO}_4^{2-}]$, of free sulphate ions, this fact should result in much lower values of E for the highest cadmium concentration than for the lowest one at the same c_{SO_4} . Thus the measurements cannot be explained by assuming only mononuclear complexes to exist in the solutions. (*Cf.* 4, p. 75, Fig. 6.)

At sufficiently small concentrations of cadmium the polynuclear complexes disappear and simultaneously $[\text{SO}_4^{2-}]$ approaches c_{SO_4} . In the limit case $c_{\text{Cd}} = 0$ and $[\text{SO}_4^{2-}] = c_{\text{SO}_4}$, and owing to the small variation of E at constant c_{SO_4} and changing c_{Cd} the extrapolation

* The generalized Bodländer equation has been used in several forms by Bjerrum¹², Frønaeus¹, p. 15, and Leden⁴, p. 13; 11, p. 33; 13.

to this limit is easily done. Such extrapolated values $\lim_{c_{\text{Cd}}=0} E = E^0$ are also to be found in Table 5. From these the function $F^0(\text{SO}_4^{2-}) = 1 + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^3$ is calculated according to (15) (denotations according to ⁸)

$$E^0 = \frac{RT}{2F} \ln \lim_{c_{\text{Cd}}=0} \frac{c_{\text{Cd}}}{[\text{Cd}^{2+}]} = \frac{RT}{2F} \ln F^0(\text{SO}_4^{2-}) \tag{15}$$

Then the complexity constants can be computed as usual, e.g. by drawing

$$F_1^0(\text{SO}_3^{2-}) = \frac{F^0[\text{SO}_4^{2-}] - 1}{[\text{SO}_4^{2-}]} \quad \text{and} \quad F_2^0(\text{SO}_4^{2-}) = \frac{F_1^0[\text{SO}_4^{2-}] - \beta_1}{[\text{SO}_4^{2-}]} \tag{16} \tag{17}$$

where $[\text{SO}_4^{2-}] = c_{\text{SO}_4}$ in this limit case. The result is $\beta_1 = (8 \pm 1) \text{ C}^{-1}$, $\beta_2 = (10 \pm 10) \text{ C}^{-2}$, and $\beta_3 = (110 \pm 10) \text{ C}^{-3}$.

Table 5. The decrease of the potential of cadmium amalgam electrodes at increasing concentrations of sulphate but constant cadmium ion concentrations. Ionic strength = 3 C.

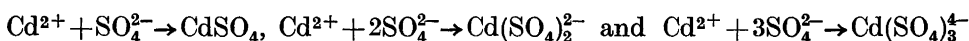
c_{SO_4} mC	$c_{\text{Cd}}=100$ mC	$c_{\text{Cd}}=33.3$ mC	$c_{\text{Cd}}=10$ mC	$c_{\text{Cd}}=3.33$ mC	$c_{\text{Cd}} = 0$		
	E mV	E mV	E mV	E mV	E^0 mV Extra- polation	$F^0(\text{SO}_4^{2-})$ (15)	$F_1^0(\text{SO}_4^{2-})$ C^{-1} (16)
0	0	0	0	0	0	1	
9.9	0.7	1.0	1.0	0.85	0.9	1.07	7.0
19.6	1.5	1.8	2.15	1.8	2.0	1.17	8.7
29.1	2.3	2.7	3.0	2.6	2.8	1.24	8.3
47.6	3.85	4.4	4.7	4.35	4.5	1.42	8.8
70.0	5.4	6.1	6.7	6.55	6.7	1.69	9.9
90.9	7.05	7.9	8.4	8.2	8.3	1.91	10.0
167	13.05	14.1	14.85	14.55	14.8	3.16	12.9
231	18.15	19.1	20.0	19.6	19.7	4.63	15.7
333	25.85	26.8	27.4	27.45	27.6	8.57	22.7
420	32.1	33	33.6	33.5	33.6	13.7	30.2
500	37.5	38.4	39.25	39.05	39.2	21.1	40.2
600	44.95	45.0	45.85	45.8	45.9	35.6	(57.7)
714	52.3	52.7	53.4	53.2	53.3	63.4	(87.4)

These complexity constants give a $F^0(\text{SO}_4^{2-})$ -curve in good agreement to the experimental points, if $c_{\text{SO}_4} < 0.5 \text{ C}$. (Cf. Fig. 1).

Hence it is possible to account for the potentiometric measurements with cadmium amalgam electrode at sufficiently small cadmium concentrations ($< \sim 5 \text{ mC}$) by assuming that the complexes CdSO_4 and $\text{Cd}(\text{SO}_4)_3^{4-}$ are formed. If the intermediate complex $\text{Cd}(\text{SO}_4)_2^{2-}$ exists at all, it has such a narrow range of existence that its complexity constant β_2 cannot possibly be computed, but no doubt $\beta_2 < 20 \text{ C}^{-2}$. At higher concentrations of cadmium, $> 5 \text{ mC}$, the results of the measurement cannot be accounted for by mononuclear complexes only.

E. DETERMINATION OF THE CONCENTRATIONS OF FREE SULPHATE IONS IN THE CADMIUM-SULPHATE SYSTEM BY THE AID OF THE SILVER-SULPHATE SYSTEM USING SILVER ELECTRODES

The measurements were still performed as potentiometric titrations with a silver-silver chloride electrode. To 20 ml solution with $c_{\text{AgClO}_4} = 0.01$ C and $c_{\text{NaClO}_4} = 2.99$ l C sodium sulphate solution was added from a burette. The result of this series is already accounted for in Table 3. The decrease of the potential of the silver electrode is also given in Table 6, here denoted E_0 . Then the same titration was repeated but now with the same cadmium concentration both in the solution in the burette and in the electrode vessel. Three such series were performed with $c_{\text{Cd}} = 10, 33.3$ and 100 mC. The decrease of the silver electrode potential is in these cases denoted E in Table 6. In these measure series the cadmium content of the solutions thus was maintained at a constant value during a titration. The silver content of the solution was decreased on account of the dilution with the titration solution, but in all solutions with the same sulphate content, the silver concentrations were equal, too. Thus all the solutions with the same sulphate and silver contents are to be found at the same horizontal line in Table 6. ΔE_{corr} in Table 6 is given as the sum of two numbers, the first of which is $E_0 - E$, and the second one is a correction that must be brought about according to the decrease of the ionic strength following from the complex formation between cadmium and sulphate ions. This correction has been obtained by the aid of the cadmium amalgam potential in the solutions, *i.e.* by interpolation in Table 5. From the figures in column E the cadmium ion concentration $[\text{Cd}^{2+}]$ can be computed from Nernst's formula (7). The difference $c_{\text{Cd}} - [\text{Cd}^{2+}]$ then signifies how much cadmium has been bound in sulphate complexes. This complex formation is firstly described by the reactions:



If the reacting concentration of cadmium is c , the decrease of ionic strength is apparently $4c$ by the first and second reaction and 0 at the third. Assuming a decrease of ionic strength equal to $4c$, we ought to obtain a m a x i m u m value of the correction. In Table 4 it has been calculated that the correction for decrease of ionic strength is 4mV/C , and from this figure and the assumed maximal decrease of ionic strength the second number in the column ΔE_{corr} has been obtained $= 4 \cdot 4c = 16(c_{\text{Cd}} - [\text{Cd}^{2+}])$ mV (concentrations in C). From the values of ΔE_{corr} the sulphate amount, $\Delta[\text{SO}_4^{2-}]$, bound in cadmium complexes has been computed from (13).

Table 6. Determination of $\Delta[\text{SO}_4^{2-}]$ and the ligand number \bar{n} of the cadmium-sulphate system by measurements with a silver-silver chloride electrode.

$c_{\text{Cd}} = 0$ (Cf. Table 3)				$c_{\text{Cd}} = 10 \text{ mC}$				$c_{\text{Cd}} = 33.3 \text{ mC}$				$c_{\text{Cd}} = 100 \text{ mC}$					
c_{Ag} mC	c_{SO_4} mC	$[\text{SO}_4^{2-}]_0$ mC	E_0 mV	E mV	ΔE_{corr} mV	c^* mC	$\Delta[\text{SO}_4^{2-}]$ mC	E mV	ΔE_{corr} mV	c^* mC	$\Delta[\text{SO}_4^{2-}]$ mC	\bar{n}	E mV	ΔE_{corr} mV	c^* mC	$\Delta[\text{SO}_4^{2-}]$ mC	\bar{n}
							(13)				(13)	(18)				(13)	(18)
10	0	0	0	0	0							□					+
9.76	24.4	24.0	1.7	1.7	0	1											
9.52	47.6	46.8	3.4	3.3	0.1+0.0	3	2	3.3	0.1+0.1	9	4	0.12	3.1	0.3+0.4	26	16	0.16
9.30	69.8	68.7	5.1	4.9	0.1+0.1	4	4										
9.09	90.9	89.5	6.6	6.5	0.1+0.1	5	4	6.3	0.3+0.2	15	11	0.33	6.0	0.6+0.6	35	26	0.26
8.69	130.5	129	9.4	9.3	0.1+0.1	6	4	9.0	0.4+0.3	19	16	0.48	8.6	0.8+0.7	42	33	0.33
8.33	167	165	12.1	12.0	0.1+0.1	7	4	11.6	0.5+0.3	22	18	0.54	11.1	1.0+1.0	64	45	0.45
8.00	200	198	14.6	14.5	0.1+0.1	7	4	14.3	0.3+0.4	24	16	0.48	13.5	1.1+1.1	70	49	0.49
7.41	259	256	19.1	19.0	0.0+0.2	8	4	18.7	0.4+0.4	27	18	0.54	17.8	1.3+1.3	79	59	0.59
6.67	333	330	24.8	24.8	0.0+0.2	9	5	24.3	0.5+0.5	29	23	0.69	23.4	1.4+1.4	87	65	0.65
5.71	428	425	32.7	32.7	0.0+0.2	9	5	32.0	0.7+0.5	30	29	0.87	31.0	1.7+1.5	92	76	0.76
5.00	500	497	39.1	39.1	0.0+0.2	10	5	38.1	1.0+0.5	31	33	(1.0)	37.2	1.9+1.5	95	83	0.83

* $c = c_{\text{Cd}} - [\text{Cd}^{2+}]$, where $[\text{Cd}^{2+}]$ has been obtained from the values of E in Table 5 from (7).

The result of this calculation shows that $\Delta[\text{SO}_4^{2-}]$ in all cases is less than $c_{\text{Cd}} - [\text{Cd}^{2+}]$, e.g. the quotient $\frac{\Delta[\text{SO}_4^{2-}]}{c_{\text{Cd}} - [\text{Cd}^{2+}]} = \nu < 1$. If the complexes between cadmium and sulphate ions were CdSO_4 and $\text{Cd}(\text{SO}_4)_3^{4-}$, the quotient ν would have to stay within the range $1 < \nu < 3$, and in the solution at the bottom of Table 6 ν ought to have reached a value of about 2.5. It is true that the relative error of $\Delta[\text{SO}_4^{2-}]$ might be rather considerable, particularly according to the uncertain correction for the decrease of ionic strength, but on the other hand it seems rather incredible that the error can be so large that only one third of the correct value should be obtained, e.g. an error of 200 %, all the more as the experimental values of ΔE_{corr} and thus of $\Delta[\text{SO}_4^{2-}]$ are already corrected maximally upwards.

Nor can the discrepancy be explained by the formation of polynuclear complexes. A value of $\nu < 1$ means that in such complexes, $\text{Cd}_m(\text{SO}_4)_n^{2(m-n)}$, m should on an average be greater than n , but that is contradicted by the generalized Bodländer equation used on the potentials of the cadmium amalgam electrodes in Table 5 (cf. ⁴, p. 75) and the limit function $F^0(\text{SO}_4^{2-})$ also calculated in Table 5. A quantitative scrutiny of the results of Tables 5 and 6 gives as

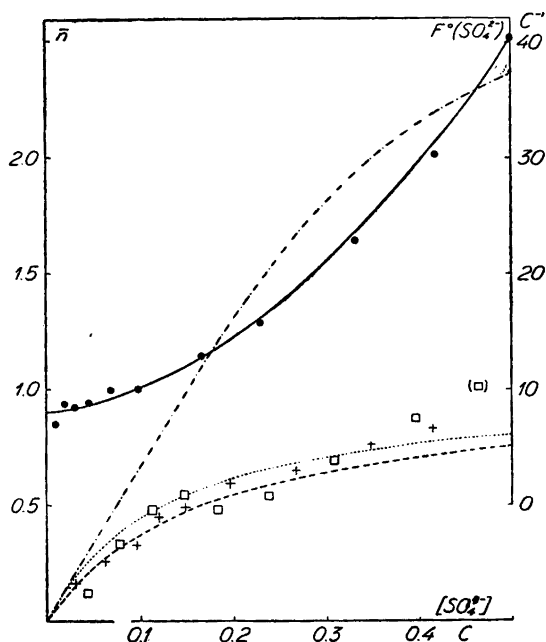


Fig. 1. The functions \bar{n} and $F_1^0(\text{SO}_4^{2-})$ of the cadmium-sulphate system.

Solid curve: $F_1^0(\text{SO}_4^{2-}) = 8 + 10 [\text{SO}_4^{2-}] + 110 [\text{SO}_4^{2-}]^2$

● $F_1^0(\text{SO}_4^{2-}) = \frac{F^0(\text{SO}_4^{2-}) - 1}{c_{\text{SO}_4}}$, where $F^0(\text{SO}_4^{2-})$ is calculated from (15).

Cf. Table 5.

Dashed-dotted curve: $\bar{n} = \frac{8[\text{SO}_4^{2-}] + 20[\text{SO}_4^{2-}]^2 + 330[\text{SO}_4^{2-}]^3}{1 + 8[\text{SO}_4^{2-}] + 10[\text{SO}_4^{2-}]^2 + 110[\text{SO}_4^{2-}]^3}$, three complexes provided

Dotted ($\beta_1 = 8$) and dashed ($\beta_1 = 6$) curves: $\bar{n} = \frac{\beta_1[\text{SO}_4^{2-}]}{1 + \beta_1[\text{SO}_4^{2-}]}$, one complex provided.

□ and + : $\bar{n} = \frac{\Delta[\text{SO}_4^{2-}]}{c_{\text{Cd}}}$ for $c_{\text{Cd}} = 33.3$ resp. 100 mC. Cf. Table 6.

result, that there cannot be found any complex system, which satisfies the measured values of both the tables. Probably this negative result will remain, even though it were possible to correct the potentials in Table 5 for the decrease of ionic strength, a correction that cannot be done, however, as long as the complex system is not unravelled.

From the values $\Delta[\text{SO}_4^{2-}]$ in Table 6 the formation function \bar{n} for the cadmium-sulphate system, defined by (18), can be computed

$$\bar{n} = \frac{\Delta[\text{SO}_4^{2-}]}{c_{\text{Cd}}} \quad (18)$$

This calculation has been made for the two highest cadmium concentrations in Table 6. In Fig. 1 the values obtained have been plotted together with the formation curve, which is arrived at by assuming only one complex to be built up in the solutions, *viz.* the uncharged compound CdSO_4 , with a complexity constant $\beta_1 = 8 \text{ C}^{-1}$. As a comparison the complexity curve for $\beta_1 = 6 \text{ C}^{-1}$ has also been drawn in Fig. 1. Thus the curves represent the functions

$$\bar{n} = \frac{\beta_1[\text{SO}_4^{2-}]}{1 + \beta_1[\text{SO}_4^{2-}]} \quad (19)$$

for these two values of β_1 . As is seen from Fig. 1 the experimental values are rather well gathered along a curve of this type. For the sake of comparison that \bar{n} -curve is also drawn in Fig. 1 that is obtained from the complexity constants, computed from the measurements with cadmium amalgam electrodes in Table 5.

The measurements of sulphate ion concentration with the silver electrode thus give the result that only one complex is formed in the solution, *viz.* the uncharged molecule CdSO_4 , and that the complexity constant of the same is $\beta_1 = (7 \pm 2) \text{ C}^{-1}$. This value coincides within the errors of experiments with the value of $\beta_1 = (8 \pm 1) \text{ C}^{-1}$, computed from the measurements with cadmium amalgam electrodes.

F. DISCUSSION OF THE RESULTS OF THE MEASUREMENTS

The most reasonable explanation of the divergent results between the measurements with cadmium amalgam and silver electrodes seems to be the following one. By the calculation of the complexity constants from the measurements with cadmium amalgam electrodes, it has been assumed that the ionic environment can be regarded as unchanged when monovalent perchlorate ions are exchanged for divalent sulphate ions, so that the activity factor of the cadmium ion maintains a constant value during a titration. It is, however, rather probable that this assumption does not hold good. In solutions without a neutral salt two ions with opposite electrical charges are supposed to form associated ion pairs, an association starting at very small concentrations in aqueous solutions, if the ions are divalent (*vide* Bjerrum¹⁴ or Güntelberg⁶). The decrease of activity factors at increasing concentrations is thus interpreted as a stabilization of the ion pair. Analogously the increase of the $F_1^0(\text{SO}_4^{2-})$ -function, which has been formally interpreted as a formation of essentially the complex $\text{Cd}(\text{SO}_4)_3^{4-}$ in part D of this paper, is perhaps instead a measure of increasing stability of the associated ion pair $\text{Cd}^{2+}\text{SO}_4^{2-}$, so that the increase of $F_1^0(\text{SO}_4^{2-})$ has to be interpreted as an increase of the complexity "constant"

β_1 for this ion pair at increasing sulphate concentrations and not as a proceeding complex formation in a step system. The function $F_1^0(\text{SO}_4^{2-})$ is maintained at a constant value, as long as $c_{\text{SO}_4} < \sim 60$ mC and at these small sulphate concentrations it ought thus to be possible to calculate with constant activity conditions in the solutions, if the cadmium content is also sufficiently small. This way of looking at the matter corresponds to the results of those authors (for literature, *vide* ⁴), who have investigated cadmium sulphate solutions without adding a neutral salt and then have found a very strong complex formation ($\beta_1 \simeq 200 \text{ C}^{-1}$). That would mean that there should appear a strong association already at much smaller concentrations of divalent ions in such solutions. It may also be observed that the authors (for literature, *vide* ⁴), who have found the cadmium sulphate completely dissociated, calculate with activity factors in a manner which according to Bjerrum ¹⁴ (*cf.* Güntelberg ⁴, p. 26) is tantamount to the assumption of associated ion pairs. In solutions of pure cadmium sulphate, not too concentrated, the activity factors of the two ions ought to be about equal, but in the solutions studied in this paper, where c_{SO_4} is mostly much greater than c_{Cd} , it is more probable that the activity factor of the cadmium ion is more influenced by the exchange of perchlorate for sulphate than the activity factor of the sulphate ion, as it is commonly supposed that an exchange of negative ions in an ionic environment influences more the activity factor of a positive ion than that of a negative one *. From this point of view the emfs in Table 6 are more to be considered as the result of a change of the activity factor of the cadmium ions caused by the increasing sulphate ion concentration than as the result of a complex formation. Hence it is also obvious, why the emf are mainly dependent on the total sulphate concentration c_{SO_4} , as the main part of the sulphate ions remain "free", even if the cadmium content of the solution is increased.

The proposed interpretation of the measurements of cadmium sulphate solutions diverges greatly from the common opinion of a complex system built up stepwise by successive complex compounds. This interpretation has been necessitated by the results of the measurements of sulphate ion concentration by the aid of the silver-sulphate system. Thus it seems convenient to discuss some objections that might be made to these measurements.

* If the activity factors of the cadmium and sulphate ions were about equal, the function \bar{n} of the cadmium-sulphate system ought to be described by the equation

$$\bar{n} = \frac{F_1^0(\text{SO}_4^{2-}) \cdot [\text{SO}_4^{2-}]}{1 + F_1^0(\text{SO}_4^{2-}) \cdot [\text{SO}_4^{2-}]} \quad (20)$$

This curve is mainly of the same type as (18), but the experimental values of \bar{n} in Table 6 do not agree so well with (20) as with (18).

Firstly, the influence of quantitative changes of the ionic strength owing to the formation of complexes (or ion pairs). The correction for this source of error is, it is true, uncertain, but as is already mentioned, it is not easy to see how the correction set about could be made greater, which were necessary, if the measurements should be able to result in complexes of the type $\text{Cd}(\text{SO}_4)_3^{4-}$.

It is rather more difficult to judge the influence on the potential of the silver electrode because of qualitative changes of the ionic environment, that are caused by the exchange of sodium for cadmium and sulphate for perchlorate. But this source of error ought to be outbalanced as the emf used in the calculation of $\Delta[\text{SO}_4^{2-}]$ in Table 6 is the difference between the potential of two silver electrodes, both of which are dipping in solutions, with the same total concentration of sulphate ions, which owing to their negative charges ought to have the greatest influence on the activity factor of the silver ion, and it does not seem very probable that an exchange of the positive ions cadmium for sodium should be able to affect the activity factor of the silver ion with an amount corresponding to a change of the electrode potential by several millivolts.

The emfs in Table 6 used for the calculations are very small, but parallel series demonstrate that they can practically always be reproduced with an accuracy of 0.1 mV, and this accuracy ought to be sufficient for the conclusions drawn.

Finally there is the possibility that complexes of the type $\text{Ag}_p\text{Cd}_m(\text{SO}_4)_n^{p+2m-2n}$ are formed in the solutions. If this is the case it is not possible to make a simple computation of the complexes of the cadmium-sulphate system. But as there is no sign of polynuclear complexes in the silver-sulphate system and as, according to the opinion of the present author, the cadmium-sulphate system is most probably best described by assuming it to contain the ion pair $\text{Cd}^{2+}\text{SO}_4^{2-}$ as the only "complex", there are no strong arguments for assuming such complicated complexes to have been built up in sulphate solutions containing both silver and cadmium ions.

On the other hand there are many reasons that argue in favour of the result, obtained from the measurements with silver electrodes, *i.e.* that only one complex (associated ion pair) exists in solutions of 2-2-sulphates. Firstly the remarkable uniformity of the qualities of these electrolytes, already mentioned in the introduction of the present paper, which speaks in favour of complex compounds of the same sort in all solutions of 2-2-sulphates and thus suggests fairly simple conditions in all of them. The formation of associated ion pairs is mostly the result of electrostatic forces, which do not too much depend on individual qualities of the ions. The fact that the decrease

of the electrode potential in solutions of cadmium perchlorate, to which sulphate is added, becomes about the same independent of the initial cadmium ion concentration, suggests an activity influence from the sulphate ions rather than a complex formation. Finally some experiments with an anion exchange resin¹⁵ also speak in favour of the absence of anionic complexes in the cadmium-sulphate system.

If this simplification of the complex chemistry of 2—2-sulphates is correct, it ought to be possible to describe their solutions mainly in terms of activity factors, and judging from the uniform conditions of the electrolytes it might be expected that the equations of a theory for these electrolytes will not need to contain too many parameters, not even in equations valid for rather concentrated solutions.

SUMMARY

1. Potentiometric measurements with silver electrodes in the silver-sulphate system can be accounted for by assuming that the complexes AgSO_4^- and $\text{Ag}(\text{SO}_4)_2^{3-}$ are formed in the solutions. The complexity (concentration) constants are $\beta_1 = (1.7 \pm 0.05) \text{ C}^{-1}$ and $\beta_2 = (1.9 \pm 0.1) \text{ C}^{-2}$, if the ionic strength is maintained constant = 3 C (NaClO_4), and $\beta_1 = (1.7 \pm 0.05) \text{ C}^{-1}$ and $\beta_2 = (1.0 \pm 0.1) \text{ C}^{-2}$ if the concentration of sodium ions = 3 C.

2. The same measurements also give as a result that the potential of a silver electrode is increased by 4 mV/C, when the ionic strength, 3 C, is increased by adding more sodium perchlorate.

3. Potentiometric measurements with cadmium amalgam electrodes in the cadmium-sulphate system can be accounted for by assuming the complexes CdSO_4 , $(\text{Cd}(\text{SO}_4)_2)^{2-}$ and $\text{Cd}(\text{SO}_4)_3^{4-}$ to be formed, if the cadmium content of the solutions $< \sim 5 \text{ mC}$. The complexity constants are computed to $\beta_1 = (8 \pm 1) \text{ C}^{-1}$, $\beta_2 = (10 \pm 10) \text{ C}^{-2}$, and $\beta_3 = (110 \pm 10) \text{ C}^{-3}$. These results are obtained on the assumption that the ionic environment can be regarded as constant for all the solutions investigated. This assumption seems to be dubious judging from the following measurements. At cadmium contents $> 5 \text{ mC}$ the mononuclear complexes, just mentioned, are not sufficient to account for the measurements with cadmium amalgam electrodes.

4. A method of determining concentrations of the free ligand by the aid of a known complex step system is described.

5. This method has been used to determine the concentration of free sulphate ions in the cadmium-sulphate system by the aid of the known silver-sulphate system using silver electrodes. The result of this determination is, that only one complex compound exists in the cadmium-sulphate system,

viz. the uncharged molecule or associated ion pair CdSO_4 . Its complexity constant is $\beta_1 = (7 \pm 2) \text{ C}^{-1}$ in good agreement with the results from measurements with cadmium amalgam electrodes.

6. The nonagreement of 3 and 5 in this summary can be explained in the following way. The result from 3 has been obtained by assuming that the increase of the function $F_1^0(\text{SO}_4^{2-})$ is a consequence of a successive complex formation at increasing sulphate concentrations. But this increase might also be explained by a change of the activity coefficient of mainly the cadmium ion, when perchlorate is exchanged for sulphate. The activity conditions can only be regarded as constant, when the sum of cadmium and sulphate ion concentration $< 60 \text{ mC}$. Such a change of the activity factors can also be described as a formation of associated ion pairs, which are also formed at much lower concentration if the solutions contain no other ions than cadmium and sulphate.

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REFERENCES

1. Fronaeus, S. Diss. (1948) 57. Lund.
2. Fronaeus, S. *Acta Chem. Scand.* **4** (1950) 72.
3. Näsänen, R. *Acta Chem. Scand.* **3** (1949) 179.
4. Leden, I. Diss. (1943) 73. Lund.
5. Plake, E. *Z. physik. Chem. A* **172** (1935) 113.
6. Güntelberg, E. Diss. (1938) 13. Copenhagen.
7. Hass, K., and Jellinek, K. *Z. physik. Chem. A* **162** (1932) 172.
8. Leden, I. *Svensk Kem. Tid.* **58** (1946) 130.
9. Leden, I. *Acta Chem. Scand.* **3** (1949) 1318.
10. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
11. Leden, I. *Svensk Kem. Tid.* **56** (1944) 36.
12. Bjerrum, J. Diss. (1941) 29. Copenhagen.
13. Leden, I. *Z. physik. Chem. A* **188** (1941) 165.
14. Bjerrum, N. *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.* **7** (1926) no. 9.
15. Leden, I. *Svensk Kem. Tid.* **64** (1952) 145.

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