[CONTRIBUTION NO. 358 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution and Heat Contents of Aqueous Cadmium Sulfate Solutions

BY T. H. DUNKELBERGER[1,2] AND A. L. ROBINSON

This investigation was carried out to extend the temperature range of heat of dilution measurements of aqueous cadmium sulfate solutions[3,4] and to compute from such data the partial molal heat contents and heat capacities of the components of the solutions. A similar study of sodium chloride solutions[5,6] led to a verification of the limiting law of Debye and Hückel,[7,7a] while earlier studies of 2–2 type electrolyte solutions indicated large deviations from limiting law behavior at the lowest concentrations measured.[3]

The results of this investigation also may be compared with data of La Mer and Parks[8] on the electromotive force of cells containing cadmium sulfate. Activity coefficients of cadmium sulfate determined by the isopiestic vapor pressure method[9] differed appreciably from the values of La Mer and Parks, but were in good agreement with activity coefficients calculated from freezing point measurements and corrected to 25° with the aid of then available thermal data. The relative partial molal heat contents and heat capacities determined in this investigation are just the quantities required to correct freezing point measurements to 25°. These thermal quantities may also be computed from e. m. f. data so that our measurements should be of some value in locating the source of the discrepancy mentioned above.

Experimental

The apparatus was essentially that used by Gulbransen[5,10,11] with the following modifications.

New gold-plated brass pipets were constructed.[12] Their volumes were 6.285 and 6.293 ± 0.002 ml. at 20°. The pipets were filled by evacuating to the limit obtained with a good water pump and introducing the solution to be diluted under this reduced pressure.

For measuring the time current was flowing through the heating elements the automatic switches described by Lange and Monheim[13] were replaced by a hand operated switch, which opened and closed the heating circuit and at the same time started and stopped an electric stop clock. The time of heating could thus be read with an accuracy of 0.01 second.

The cadmium sulfate was purified according to the method of La Mer and Parks.[8] Analysis of the dried salt for sulfate indicated 99.82 ± 0.03% sulfate. Spectroscopic analysis indicated the absence of metallic impurities in amounts more than a few thousandths of one per cent.;[14] it is probable that the principal impurity was tenaciously retained water. All solutions were made up by weight or by the dilution of a more concentrated solution that had been made up by weight.

The experimental procedure and the method for determining the value of the heat effect accompanying a dilution were the same as previously described.[5,10,11,13]

Experimental Results

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The remainder of the table indicates the number of duplicate runs, the average value of the intermediate heat of dilution (ΔH)[15] and the probable error, exclusive of systematic errors, at each temperature. Although the absolute values of the probable errors are larger than those observed in the study of sodium chloride solutions,[5] the percentage errors are of the same magnitude. It is estimated that systematic errors are not greater than 1%.

Extrapolation to Infinite Dilution.—The data of Table I are plotted against $m^{1/2}$ in Figs. 1 and 2 by the point to point method previously described.[11] The lowest point on the 15° curve was obtained after a smooth curve had been drawn through the other experimental points at that temperature by placing the $m = 0.0125$ point on the smooth curve.

Lange and his collaborators have found that in very dilute solutions the relation between the heat of dilution and $m^{1/2}$ is linear within es-

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[1] From a thesis submitted by Mr. T. H. Dunkelberger in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1937.

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[3] E. Lange, J. Monheim and A. L. Robinson, THIS JOURNAL, **55**, 4733 (1933).

[4] E. Plake, *Z. physik. Chem.*, **162A**, 257 (1932).

[5] E. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

[6] T. F. Young and W. L. Groenier, *ibid.*, **58**, 187 (1936).

[7] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

[7a] H. Bjerrum, *Z. physik. Chem.*, **119A**, 145 (1926).

[8] V. K. La Mer and W. G. Parks, THIS JOURNAL, **55**, 4343 (1933).

[9] R. A. Robinson and R. S. Jones, *ibid.*, **58**, 959 (1936).

[10] E. Gulbransen, Thesis, University of Pittsburgh, 1934.

[11] E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

[12] T. H. Dunkelberger, Thesis, University of Pittsburgh, 1937.

[13] E. Lange and J. Monheim, *Z. physik. Chem.*, **149A**, 51 (1930).

[14] Thanks are due to Dr. Mary Warga and Mr. Marcus Morgan for making this examination.

[15] Where possible the nomenclature of Lewis and Randall "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, is used.

TABLE I

$-\Delta H$, cal./mole $CdSO_4$

m_1	m_2	Runs	10°	Runs	15°	Runs	20°
0.8	0.005031	4	515 ± 4			6	968 ± 8
.8	.01003	4	415 ± 6			6	837 ± 8
.4	.002516	4	568 ± 4	4	868 ± 14	6	987 ± 4
.4	.005015	6	500 ± 2	4	762 ± 8	4	852 ± 5
.2	.001258	4	616 ± 4	4	896 ± 11	4	992 ± 8
.2	.002508	4	546 ± 6	6	796 ± 5	4	874 ± 10
.1	.0006289	4	667 ± 8	4	820 ± 8	2	994 ± 1
.1	.001254	6	587 ± 3	4	731 ± 8	4	889 ± 5
.05	.0003144	4	618 ± 6	4	785 ± 11	4	879 ± 10
.05	.0006269	6	569 ± 7	4	711 ± 15	6	813 ± 10
.025	.0001572	8	562 ± 7	4	688 ± 6	4	763 ± 5
.025	.0003134	6	529 ± 10	4	653 ± 10	6	719 ± 9
.0125	.00007861			6	592 ± 16		

timated experimental error and have extrapolated to infinite dilution accordingly.[11] This was the procedure adopted with the sodium chloride measurements,[5] although some curvature at the greatest dilutions was noticed.[16] The chord–area method of Young and Vogel[17] is undoubtedly better for determining the initial slopes of the heat of dilution curves provided that a suitable analytical expression for the results can be found. The extrapolation to infinite dilution with our method of plotting is somewhat more uncertain and limiting slope values obtained in this manner are not of high accuracy, but our procedure is adequate for determining values for the thermal quantities desired.[18]

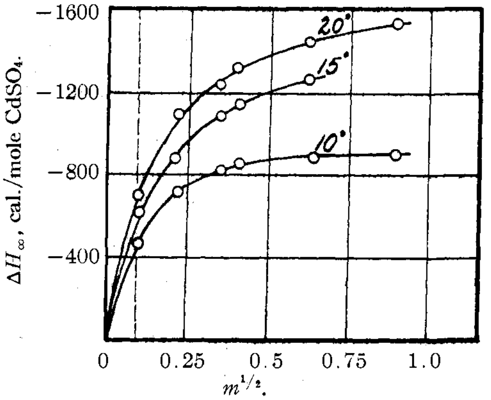

Fig. 1.—Integral heats of dilution of cadmium sulfate. The region to the left of the broken line is shown in Fig. 2.

The situation with cadmium sulfate and other 2-2 type salts[3] is complicated by the fact that the curves at the lowest measured concentrations have slopes that are considerably greater than the limiting theoretical slopes (for 1-1, 2-1, and 1-2 type salts the situation is reversed). This may be due to incomplete dissociation, complex ion formation or some other factor. In any case, agreement with theory at infinite dilution demands that the curves of Fig. 2 show inflection points at some very low concentration. Apparently our measurements have not been extended to sufficiently low concentration to reveal this effect. Although the unusually great length of our chords is a disadvantage in using the chord–area method, a plot of the chords showed no indication of a maximum slope at low concentrations. Since earlier measurements with zinc and copper sulfates[3] at 25° extending to 4.6×10^{-5} m also showed no evidence of a maximum slope,[19] we feel that a linear extrapolation

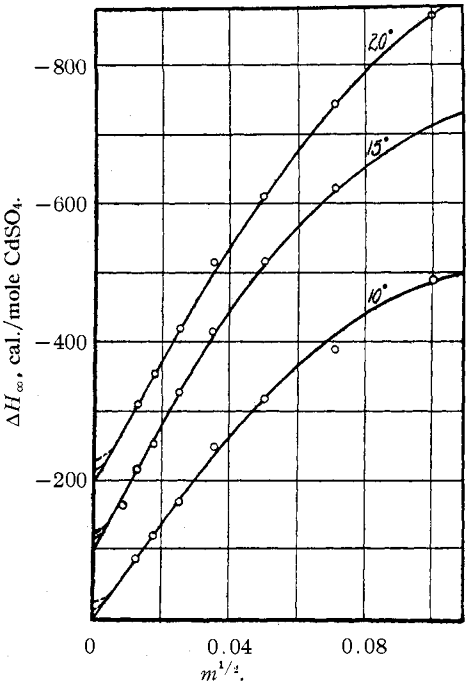

Fig. 2.—Integral heats of dilution of cadmium sulfate. The 15 and 20° curves have been displaced 100 and 200 calories, respectively.

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[16] The chord–area method applied to these data by Young and Groenier[6] gave limiting slopes in excellent agreement with theoretical values. Similar treatment of the results obtained with 8 other 1-1 type and 17 salts of the 1-2 and 2-1 valence types by Lange and his collaborators gave limiting slope values that in most cases are in better agreement with theory than the values obtained by linear extrapolation. Professor T. F. Young has kindly communicated this information.

[17] T. F. Young and O. G. Vogel, THIS JOURNAL, **54**, 3025 (1932).

[18] $\bar{L}_2$ values for sodium chloride solutions at 25° calculated by the point to point method [A. L. Robinson, *ibid.*, **54**, 1311 (1932)] and the chord–area method [T. F. Young and O. G. Vogel, *ibid.*, **54**, 3030 (1932)] are in excellent agreement although the limiting slopes reported differ considerably.

[19] Professor T. F. Young (personal communication) has found evidence for a maximum slope in the case of calcium sulfate [E. Lange and J. Monheim, *Z. physik. Chem.*, **150A**, 349 (1931)] at about 0.001 m and suggests that if the maximum is due to incomplete dissociation it might be expected to occur at still smaller concentrations with weaker salts.

of the experimental results will introduce no large error into the integral heat of dilution values, although it will not give a correct value for the limiting slope. This is evident from an inspection of Fig. 2 where several extrapolations fusing into the theoretical limiting curve are shown. We have arbitrarily added 15 cal./mole to the values for the integral heats of dilution obtained by linear extrapolation, to include probable approach to the theoretical limiting slope; this introduces a further uncertainty, of not more than 10 cal., into the values of Table III. The values of the slopes used for the linear extrapolation are given in Table II, together with theoretical values[20,21] for the limiting slopes.

TABLE II

$\partial \Delta H_\infty / \partial m^{1/2}$

t, °C.	Theor.	Lin. extrap.
10	−2840	−6330
15	−3144	−8320
20	−3472	−8800
25	−3816	−10800(3)

Integral Heats of Dilution.—An attempt to find an empirical equation to fit the curves of Fig. 1 over their entire range was unsuccessful. The section of the 10° curve above $m^{1/2} = 0.05$, however, was well represented by an equation of the type $\Delta H_\infty = A + Be^{-Cm^{1/2}}$. The same type of equation fitted the 15° curve reasonably well but was quite unsatisfactory for the 20° curve. The equations are

$$10^\circ \quad -\Delta H_\infty = 881.4 - 852.4e^{-7.36m^{1/2}} \text{ cal./mole}$$

$$15^\circ \quad -\Delta H_\infty = 1260.7 - 1173.9e^{-5.60m^{1/2}} \text{ cal./mole}$$

This type of equation has one serious defect; it has an asymptote at or near the upper concentration limit of these experiments and therefore fails to follow the experimental trend at higher concentrations, where another inflection point and sharp rise[3,22] are indicated for the curves of Fig. 1. For this reason graphical rather than analytical values were used in obtaining derived quantities for the highest concentrations of these experiments.

Table III lists values for the integral heat of dilution at rounded concentrations read from the experimental curves of Figs. 1 and 2 (extrapolated as indicated above) and also, for 10 and 15°, values calculated from the empirical equations for $m^{1/2} > 0.05$. The mean deviations of the experimental points from the graphical values are 7.5, 10.8, and 8.0 cal. for the 10, 15, and 20° curves, respectively; mean deviations of calculated values from graphical values are 5.5 and 12.7 cal. at 10 and 15°. There is little to choose between the two sets of values.

Relative Partial Molal Heat Contents.—The relative partial molal heat contents of the solvent and solute ($\bar{L}_1$ and $\bar{L}_2$) were evaluated from the equations of Rossini[23]

$$\bar{L}_1 = \frac{m^{3/2}}{2(55.508)} \frac{d}{dm^{1/2}} (\Delta H_\infty)$$

$$\bar{L}_2 = -\Delta H_\infty - \frac{m^{1/2}}{2} \frac{d}{dm^{1/2}} (\Delta H_\infty)$$

The slopes necessary for these calculations were obtained by applying the differentiated form of Lagrange's interpolation formula[24] to the curves of Figs. 1 and 2 or by differentiation of the empirical equations given above. Values for $\bar{L}_1$ and $\bar{L}_2$ so obtained are given in Table IV.

TABLE III

INTEGRAL HEATS OF DILUTION OF CADMIUM SULFATE SOLUTIONS

$-\Delta H_\infty$, cal./mole cadmium sulfate

	10°		15°		20°
m	Calcd.	Graph	Calcd.	Graph	Graph
0.0001	48	48	68	68	73
.0005	127	127	171	171	182
.001	185	185	248	248	263
.005	365	367	471	495	556
.01	473	467	590	594	688
.05	717	718	924	907	1035
.1	798	816	1061	1020	1179
.2	850	845	1162	1171	1302
.4	873	867	1232	1257	1435
.8	880	882			1524

Relative Partial Molal Heat Capacity.—To evaluate $\bar{C}_{p_2} - \bar{C}^\circ_{p_2}$ values of $\bar{L}_2$ were plotted against t for each of a number of round concentrations and the slopes of the resulting curves were determined. Values for $\bar{L}_2$ at 25° were taken from the results of Lange, Monheim and Robinson.[3] Figure 3 shows some typical plots. For the short temperature range of these studies (10–25°) a linear variation of $\bar{L}_2$ with temperature was assumed and the straight lines best representing the results were derived by the method of least squares.

The dilution measurements of Plake,[4] although made with a less sensitive calorimeter and under less carefully controlled conditions, are of some

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[20] O. Gatty, *Phil. Mag.*, **11**, 1082 (1931).

[21] G. Scatchard, THIS JOURNAL, **53**, 2037 (1931).

[22] H. B. Holsboer, *Z. physik. Chem.*, **39**, 691 (1901).

[23] F. D. Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

[24] T. R. Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, N. Y., 1917.

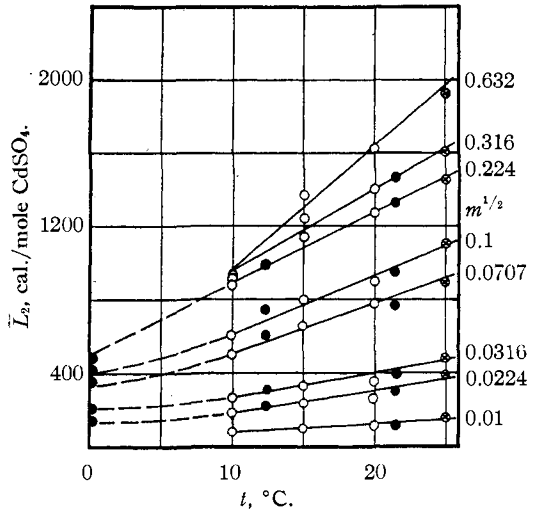

Fig. 3.—$\overline{L}_2$ *vs. t.* ●, Plake; ⊗, Lange, Monheim and Robinson; ○, this investigation.

interest for purposes of comparison. At about 21.3° Plake measured heats of dilution between 0.25 and 0.0002 *M*; a few measurements were made at about 12.2 and 0.3° between 0.1 and 0.005 *M*. These results were plotted by the point to point method and after extrapolation to infinite dilution $\overline{L}_2$ values were calculated as indicated above. These values are shown in Fig. 3 although they were not used in computing the $\overline{L}_2$ *vs. t* slopes. It is interesting to note that the most reliable of Plake's $\overline{L}_2$ values (21.3°) are in good agreement with our results. The $\overline{L}_2$ values for 12.2 and 0.3° are uncertain to about 100 cal./mole because of the long extrapolation to infinite dilution so that the departures from linearity indicated in Fig. 3 cannot be taken seriously.

TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF CADMIUM SULFATE SOLUTIONS

m	$\overline{L}_2$, cal./mole CdSO₄ 10°	15°	20°	$\overline{L}_1$, cal./mole H₂O 10°	15°	20°
0.0001	67	92	101	-0.0_435	-0.0_439	-0.0_479
.0005	168	225	239	$-\ .0_338$	$-\ .0_343$	$-\ .0_387$
.001	254	316	337	$-$ .0011	$-$ .0012	$-$ .0025
.005	486	639	765	$-$ .010	$-$ .013	$-$ .019
.01	588	786	890	$-$ .027	$-$ .032	$-$ .036
.05	851	1129	1259	$-$ .120	$-$ .187	$-$ .188
.1	893	1234	1387	$-$ .174	$-$ .318	$-$ .475
.2	902	1295	1498	$-$ .188	$-$ .437	$-$ .765
.4	908	1357	1612	$-$ .262	$-$ .722	-1.64
.8	913		1716	$-$ .483		-4.23

The slopes of the curves of Fig. 3 are plotted against $m^{1/2}$ in Fig. 4. The theoretical limiting slope[25,26] for 25°, 106 cal. mole^{-1} degree^{-1}, is also shown. Values for $\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ read from the smoothed curve are given in Table V.

TABLE V

RELATIVE PARTIAL MOLAL HEAT CAPACITY OF CADMIUM SULFATE

m	$\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ cal./mole °C.	m	$\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ cal./mole °C.
0.0001	5	0.05	41
.0005	12	.1	46
.001	15	.2	55
.005	26	.4	66
.01	31	.8	79

Discussion

Calorimetric values for integral heats of dilution and relative partial molal heat contents may be compared with values obtained electrometrically by La Mer and Parks.[8] Evaluation of $\overline{L}_2$ values from calorimetric data involves a differentiation of experimental results with respect to concentration; hence, values for integral heats of dilution should be more reliable. Evaluation of $\overline{L}_2$ from e. m. f. measurements similarly requires a differentiation of the experimental results with respect to temperature, while the determination of integral heats of dilution requires the subsequent integration of these $\overline{L}_2$ values over a range of concentrations; hence, the integral heats of dilution should be less reliable than the $\overline{L}_2$ values. Therefore, a comparison of $\overline{L}_2$ values is made, in Table VI, although our ΔH_∞ values should be somewhat more reliable.

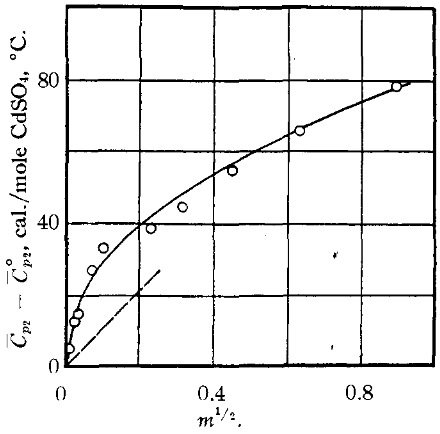

Fig. 4.—$\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ *vs.* $m^{1/2}$.

It is noted that the agreement is excellent at the lower concentrations listed but the differences at higher concentrations are greater than

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(25) M. Randall and F. D. Rossini, THIS JOURNAL, **51**, 323 (1929).

(26) V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **55**, 1004 (1933)

the estimated experimental errors. The most dilute solution used in the e. m. f. measurements was 0.0005 *m*, while our measurements extend to about 0.0001 *m;* La Mer and Parks extrapolated to infinite dilution with the aid of the extended Debye–Hückel theory, while our somewhat shorter, semi-empirical extrapolation has been described above. Since the agreement is excellent at the lowest concentrations it is evident that the discrepancies at higher concentrations are not due to the different methods of extrapolation. Since La Mer and Parks have indicated the existence of certain experimental difficulties with their cells and since activity coefficients calculated from their data do not agree well with those found by Robinson and Jones[9] it seems likely that some part of the discrepancy is due to unreliability of the e. m. f. measurements. Moreover, Harned,[27] by recalculating similar data obtained by La Mer and Cowperthwaite[28] with zinc sulfate cells, has found that the method of calculation used by La Mer and Cowperthwaite introduces uncertainties aside from those inherent in the experimental work.

TABLE VI

	$\overline{L}_2$, cal./mole $CdSO_4$					
	10°C.		15°C.		20°C.	
m	Cal.	E. m. f.	Cal.	E. m. f.	Cal.	E. m. f.
0.0001	67	—	92	—	101	—
.0005	168	147	225	182	239	239
.001	254	234	316	276	337	327
.005	486	475	639	522	765	581
.01	588	568	786	650	890	740
.02	730	849	943	981	1037	1148

We have not recalculated activity coefficients for cadmium sulfate solutions at 25° by correcting freezing point data with the $\overline{L}_2$ and $\overline{C}_{p_2} - \overline{C}^\circ_{p_2}$ values reported here. Our measurements may be combined with the earlier, and probably less reliable, heats of solution measurements of Holsboer,[22] which extended from about 0.2 *m* to saturation at several temperatures, to compute relative heat contents and heat capacities for the entire concentration range from infinite dilution to saturation. Values for $\overline{C}^\circ_{p_2}$ also could be obtained by utilizing Holsboer's data. It is hoped to carry out these calculations in the near future.

We are grateful to the National Research Council for two grants in aid which made possible the construction of the apparatus used in this investigation.

Summary

Intermediate heats of dilution of aqueous cadmium sulfate solutions have been measured over the concentration range from 0.8 to 0.0001 *m* at 10, 15, and 20° and have been extrapolated to infinite dilution to obtain integral heats of dilution. No definite approach to the limiting law of Debye and Hückel is indicated at the lowest concentrations measured.

Relative partial molal heat contents and heat capacities have been calculated for the temperature and concentration ranges of the measurements and have been compared with values obtained from e. m. f. measurements by La Mer and Parks.

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[27] H. S. Harned, THIS JOURNAL, **59**, 360 (1937).

[28] V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **53**, 2040 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

A Thermodynamic Study of the Cadium–Antimony System

BY HARRY SELTZ AND B. J. DEWITT

The phase equilibrium relations in the cadmium–antimony system have been studied by several investigators.[1] Thermal, microscopic, X-ray and conductivity methods have been employed. Hansen,[2] from a critical review of these data, accepts the diagram of Murakami and Shinagawa which will be used in several calculations in this paper. Two intermetallic compounds are formed, CdSb and Cd_3Sb_2. The former is stable to its melting point, 455°, while the latter is metastable at all temperatures and melts at 420°.

In pursuance of a program of investigation of the thermodynamics of metal systems, this paper describes the results of an electromotive force study of liquid cadmium–antimony solutions.

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(1) Kurnakov and Konstantinov, *Z. anorg. Chem.*, **58**, 1 (1908); Treitschke, *Z. anorg. allgem. Chem.*, **50**, 217 (1906); Murakami and Shinagawa, *Kinzoku no Kenkyu*, **5**, 283 (1928).

(2) M. Hansen, "Der Aufbau der Zweistofflegierungen," Verlag von Julius Springer, Berlin, Germany, 1936.