On the basis of work published from this Laboratory on the activity coefficients of dilute uni-univalent chlorides,[1-3] we are convinced that such a procedure results in equations which fail to hold for low concentrations. The inadequacy of various extensions of the Debye–Hückel equation for dilute lanthanum chloride solutions has, in addition, been discussed in this paper. However, the serious discrepancy between Mason's and our activity coefficient scales is due to his method of computation and not to inconsistency in the experimental work. The osmotic coefficient, ϕ, is related to the activity coefficient, γ, by the equation

$$\phi = 1 + \frac{1}{m}\int_0^m m \, d\log_e \gamma \qquad (7)$$

To compare our activity coefficient values with Mason's measurements we have evaluated the integral in equation (7) analytically, using equation (6). The resulting equation is

$$\phi = 1 - 1.749\sqrt{m} + 3.673m \qquad (8)$$

from which we can compute values of osmotic coefficients corresponding to our measurements on the basis of the activity coefficient scale implied in equations (4), (5) or (6).

Figure 2 shows a graph of osmotic coefficient values, ϕ, plotted against the square root of the molal concentration, $\sqrt{m}$. Mason's measurements appear as the black circles in this figure, whereas the open circles correspond to our values. It is evident that a smooth curve could readily be drawn through both sets of points. The solid and dotted curves in the figure correspond to Mason's smoothed values and our equation (8),
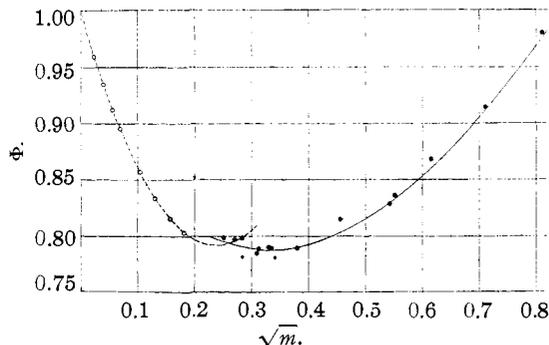
Fig. 2.

respectively. It is clear that equation (8) should not be used beyond a concentration of about 0.05 molal. The two sets of data, based on very different experimental methods, appear, however, to be quite consistent.

Summary

Measurements have been made on the potentials of lanthanum chloride concentration cells with transference from $C = 0.0006$ to 0.0333 mole per liter at 25°. From these data and accurate transference numbers, activity coefficients have been computed. The results do not appear to be in harmony with the available equations based on the interionic attraction theory since the values decrease less rapidly with increasing concentration than the theory predicts. Osmotic coefficients obtained from our results have been shown to be consistent with recent isopiestic measurements.

The Specific Heats at Low Temperatures of Manganese, Manganous Selenide, and Manganous Telluride[1]

BY K. K. KELLEY[2]

In two earlier papers[3,4] from the Metallurgical Fundamentals Section, Metallurgical Division, Bureau of Mines, data were reported for the specific heats at low temperatures of manganous oxide and manganous sulfide. Both of these substances behave anomalously, the manganous oxide having a high "hump" in its specific heat curve around 116°K. and the manganous sulfide having a two-cusped "hump" in the region around 140°K. It was thought worth while to extend these measurements to the selenide and telluride, as by analogy these substances might be expected to show anomalous behavior and thus data would exist for a series of four similar but irregularly behaving compounds.

(1) Published by permission of the Director, Bureau of Mines, United States Department of the Interior. (Not subject to copyright.)

(2) Chemist, Metallurgical Fundamentals Section, Metallurgical Division, Bureau of Mines.

(3) Millar, THIS JOURNAL, **50**, 1875 (1928).

(4) Anderson. ibid., **53**, 476 (1931).

Since the first step in the preparation of the selenide and telluride required the production of a sample of manganese of adequate purity, it seemed expedient to make measurements on this substance also, especially as the heretofore accepted entropy of manganese is based on a single average specific heat measurement of Dewar,[5] as recalculated by Lewis and Gibson.[6]

Materials.—The manganese was prepared by electrolyzing a solution containing manganous sulfate and ammonium sulfate into a mercury cathode and distilling the mercury from the resulting amalgam. The amalgam on being removed from the cell was cleaned by stirring and skimming and the excess mercury squeezed out through cheese cloth, leaving a pasty material containing 4 to 5% Mn. The latter material was placed in a quartz still, evacuated to $<10^{-4}$ mm., and heated under vacuum, the temperature being kept below 275° until most of the mercury was distilled off. Then the temperature was raised to 700° and held there for several hours to promote grain growth. The last step was necessary to obtain a stable product. Material produced at around 400° was found to ignite instantly on exposure to air. This procedure was tedious, as the facilities available permitted the distillation of only some 1000 g. of amalgam at one time, so that 40-g. batches of manganese were prepared separately.

The final product was a grayish powder consisting of clumps of individual particles of 4- to 5-micron average size. Analysis gave 99.76% Mn the remainder being principally oxygen. This corresponds to 98.94% Mn and 1.06% MnO. While around 0.24% oxygen may seem a large amount it corresponds to only about 0.01% in the cleaned and squeezed amalgam and, of course, to a very much lower fraction in the amalgam before squeezing. X-Ray analysis, which was made by J. W. Ballard, Bureau of Mines, Pittsburgh, Penna., showed the material to be 99% α-Mn. The sample used in the specific heat measurements contained 112.53 g.

The manganese selenide was prepared from manganese obtained as just described and selenium purified previously by Anderson[7] for his low-temperature specific heat measurements. A quartz tube, 75 cm. long and 2.5 cm. in diameter, sealed at one end, was constricted about 50 cm. from the sealed end in such a manner that it could be used as a still and condenser. An intimate mixture of manganese and selenium, containing 50% excess selenium, was placed in the 50-cm. portion, enough material being used to one-third fill this portion. The entire tube then was evacuated to 10^{-3} mm. and sealed off. The manganese–selenium mixture was distributed uniformly in the 50-cm. portion, the tube being clamped in a nearly horizontal position. The reaction was started by a small flame held at the end of the tube. After starting, the reaction proceeded spontaneously along the tube, several seconds being required to traverse the whole 50-cm. length. The tube, still sealed, was placed in a furnace and allowed to stand for some twenty hours at temperatures increasing

from 300 to 500° to assure complete reaction. After cooling, the sealed tip was broken, the tube attached to a vacuum pump and placed in a furnace at 500° with the condenser portion out in the air, and the excess selenium distilled off. Five batches of material of about 70 g. each were so prepared. As a final precaution 5 g. of selenium was placed in the bottom of a quartz flask, to which had been sealed a tube for condensation, and the entire quantity of manganous selenide added. This selenium was allowed to distil through the bed of manganous selenide under vacuum at 500°.

The product, on analysis, was found to be 99.35% pure, based on its manganese content, and 99.48% pure, based on its selenium content. It is interesting to compare these figures with those to be expected if the previously given analysis of the manganese is accepted, 99.58% MnSe and 0.42% MnO. The agreement indicates that but little additional contamination occurred during the preparation of the selenide. The sample used in the specific heat measurements contained 304.91 g.

The manganous telluride was prepared in a manner similar to that employed for the manganous selenide, the tellurium purified by Anderson[7] being used. The aging temperature after reaction was 725° for fifteen to eighteen hours. The excess tellurium was distilled off under vacuum at temperatures reaching 730°, and the final precautionary treatment with 5% Te in the flask also was made at 730°. The product was 99.57% pure, based on analysis for tellurium. The theoretical analysis corresponding to that of the manganese is 99.68% MnTe and 0.32% MnO, again showing but little extra contamination in the preparation process. Specific heat measurements were made on a 223.83-g. sample

The Specific Heats

No changes in apparatus have been made, and the previously given description[3,8] will suffice. It should be recorded, however, that the standard cell, volt box, stop watch, and calorimeter thermocouple were checked very carefully, and the heat capacity of the empty calorimeter was redetermined over the entire temperature range 52–298°K.

The specific heat results, expressed 15° gram. calories per gram formula mass, are given in Table I and shown graphically in Fig. 1. Correction was made for the oxide content of the materials, using the data of Millar[3] for manganous oxide through which a smoothed curve was drawn ignoring the 116°K. "hump." The magnitude of this correction varies with the temperature and ranges from 0.3 to 0.7% of the manganese values, 0 to 0.4% of the manganous selenide values, and 0.1 to 0.2% of the manganous telluride values.

The specific heat curve of manganese is regular throughout the temperature range studied and needs no discussion.

(5) Dewar, *Proc. Roy. Soc.* (London), **89A**, 158 (1913).

(6) Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

(7) Anderson, *ibid.*, **59**, 1036 (1937).

(8) Anderson, *ibid.*, **52**, 2296 (1930).

TABLE I
SPECIFIC HEAT OF Mn (54.93 g.)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.7	1.364	115.0	3.995	213.0	5.646
56.8	1.533	124.1	4.229	222.5	5.746
60.3	1.735	133.2	4.445	231.5	5.803
64.0	1.952	143.0	4.650	244.1	5.918
68.0	2.176	153.5	4.858	254.4	6.005
74.8	2.544	163.1	5.019	265.8	6.082
80.4	2.844	172.9	5.165	275.0	6.129
88.2	3.130	183.2	5.311	278.1	6.147
96.9	3.500	193.1	5.444	282.0	6.190
105.8	3.755	203.3	5.538	285.9	6.179
				289.8	6.183

SPECIFIC HEAT OF MnSe (133.89 g.)

T	C_p	T	C_p	T	C_p
54.3	5.62	115.8	11.89	242.7	19.18
57.4	6.02	118.1	11.79	245.2	23.12
61.0	6.50	118.4	11.82	249.3	22.38
69.6	7.60	120.3	11.70	251.7	17.29
79.2	8.75	120.9	11.60	254.4	15.22
81.3	8.82	121.8	11.55	257.7	13.43
82.5	8.93	123.5	11.57	261.1	12.84
84.8	9.20	123.8	11.53	264.7	12.36
86.3	9.30	124.6	11.56	268.5	12.28
89.7	9.58	127.5	11.53	273.4	12.20
92.1	9.83	128.8	11.57	277.1	12.22
93.4	9.87	132.7	11.61	280.4	12.18
96.4	10.19	133.3	11.65	287.0	12.20
99.0	10.43	142.4	11.72	92.5(a)	10.18
100.3	10.53	153.1	11.87	95.9(a)	10.49
101.5	10.59	162.0	12.03	104.8(a)	11.29
102.1	10.59	171.1	12.17	113.7(a)	12.21
104.3	10.92	180.7	12.31	122.9(a)	11.76
104.4	10.88	190.6	12.50	230.3(b)	12.15
107.4	11.10	200.0	12.62	233.9(b)	12.14
108.5	11.24	209.3	12.78	237.9(b)	12.14
110.3	11.36	218.4	12.91	243.6(b)	12.19
111.0	11.33	222.3	12.90	251.4(b)	12.18
112.4	11.59	231.0	13.16	259.0(b)	12.26
113.1	11.62	237.0	13.64	266.4(b)	12.33
114.7	11.80	239.5	14.68		

SPECIFIC HEAT OF MnTe (182.54 g.)

T	C_p	T	C_p	T	C_p
54.5	6.05	127.6	11.36	281.0	15.98
58.3	6.51	136.2	11.63	286.0	16.23
62.5	6.96	144.8	11.87	289.8	16.48
66.4	7.39	153.8	12.14	293.3	16.74
70.7	7.86	162.8	12.39	295.2	17.15
75.3	8.32	172.3	12.68	297.8	17.34
81.5	8.80	181.6	12.87	298.1	17.28
82.0	8.84	190.7	13.11	301.5	17.80
85.6	9.11	199.8	13.38	304.4	18.38
86.6	9.18	208.3	13.59	307.4	18.32
95.2	9.77	217.5	13.81	310.5	15.34
100.2	10.05	227.0	14.04	313.7	14.59
104.9	10.32	236.2	14.33	316.9	14.11
109.4	10.55	245.7	14.63	320.4	13.94
113.6	10.79	255.1	14.88	323.7	13.75
117.6	11.02	264.4	15.22	327.0	13.78
119.9	11.12	273.3	15.59		
121.4	11.16	277.2	15.76		

In the case of manganous selenide there are a number of matters of interest. It may be noted in Fig. 1 that a small "hump" was found at about 116°K., the temperature at which Millar[3] observed a large "hump" in the manganous oxide specific heat curve. The writer at first was inclined to attribute this to the oxide content of the manganous selenide sample, but further consideration made this explanation appear improbable. Neither the manganese nor the manganous telluride, both of which presumably contained about the same molal content of oxide as the manganous selenide, shows any significant evidence of abnormal behavior near this point. Furthermore, the marked difference in the slopes of the portions of the manganous selenide curve lying immediately above and below this region lends weight to this transformation being a property of the manganous selenide itself rather than the effect of a relatively small amount of impurity. The behavior in the region near 116°K. was not perfectly reproducible and was, in fact, very similar to that observed by Pitzer and Smith[9] in the neighborhood of the maximum in the silver oxide specific heat curve near 30°K. After the first cooling of the manganous selenide (to 91°K.) a set of determinations was made that is marked "a" in Table I and indicated by the dotted curve in Fig. 1. These particular results never were reproduced in spite of four additional coolings in which conditions were varied. Two sets of determinations were obtained under treatment almost identical with that given the sample in the first cooling. A third set was made after cooling slowly to 94°K. from room temperature (twenty-six hours required) and aging the substance for twenty-four hours, and a fourth set after cooling only to 112°K. While minor variations are evident in the data, no such significant differences were obtained as those between the first set and any of the four subsequent sets. Above about 125°K. the results of all the sets are in agreement. It should be emphasized that no reason could be found for attributing the non-concordance of the first set of results to any misbehavior of the apparatus or measuring instruments.

Manganous selenide shows a marked abnormality centered around 247°K. Immediately above 231°K. it was observed that the rate of heat distribution in the calorimeter decreased rapidly to one-sixth or one-seventh of the value at lower

(9) Pitzer and Smith, THIS JOURNAL, **59**, 2633 (1937).

temperatures, as evidenced by the time necessary for obtaining equilibrium after energy input. This phenomenon is much too marked to be caused merely by the increase in heat capacity of the substance and must be attributed to the slowness with which this material comes to approximate thermal equilibrium in this temperature range. Above 260°K. the rate of heat distribution again became rapid and equilibrium was readily obtained. Because of this phenomenon the measurements in the range 230–260°K. may be in error by as much as 5%, and the data tabulated and plotted can be considered only as showing the gen-

Fig. 1.—The specific heats of Mn, MnSe, and MnTe in calories per gram formula mass.

eral course of the specific heat curve. Consequently, to compute accurately the entropy increment in this range, it was necessary to measure the total heat absorption between 230 and 260°K. Two measurements were made yielding 555.9 and 557.0 calories per gram formula mass, respectively. Because of the sluggishness of the heat distribution it was thought probable that the substance could be supercooled somewhat. This was tried, and after rapid cooling from room temperature to 228°K. the results marked "b" in Table I were obtained. In Fig. 1 these may be seen to fall closely on an extrapolation of the results obtained above the "hump." Further experiments showed that it was not possible to supercool the substance much below 228°K. under conditions obtainable in the specific heat apparatus.

Manganous telluride shows a "hump" with its maximum at 307°K. The specific heat of this

substance, however, is already abnormally high at 150°K., where it exceeds 12 calories per gram formula mass. It appears that the abnormal region virtually is ended at about 320°K. Determinations above 330°K. could not be made readily because of the fusibility of the paraffin that was used in filling the openings through which the thermocouples pass into the heavy block surrounding the calorimeter. The measurements above 298°K. are subject to the uncertainties involved in the necessary extrapolation of both the temperature scale and the heat capacity curve of the empty calorimeter. However, they indicate the course of the specific heat curve of manganous telluride and are not involved in the subsequent entropy calculation. No significant change in the rate of heat distribution in the calorimeter was observed in traversing the region of the maximum and an attempt at supercooling through the abnormal range was unsuccessful.

It is interesting to compare the temperatures of the "peaks" of the manganous selenide and manganous telluride curves with those of manganous oxide and manganous sulfide. This is done in the inset in Fig. 1 where the highest "peak" temperatures are plotted against the atomic numbers of the atoms combined with manganese. There is admittedly no reason for plotting in this manner, but the plot does show that the temperature of the "peak" shifts upward in a fairly regular manner as the atomic number or mass of the combining atom increases in this series of substances.[10]

The Entropies

The results of the entropy calculations are given in Table II. For extrapolating the manganese data the Debye function of $\Theta = 344$, which fits the experimental data between 53 and 115°K., was used. For the manganous selenide, the sum

(10) The question was raised by the referee of this paper as to whether these abnormalities are inversions, characterized by a change of crystal form, or merely regions of abnormally high specific heat. The latter is almost certainly correct, although no actual measurements to prove this point have been made for manganous selenide and manganous telluride. For manganous oxide and sulfide, Ellefson and Taylor, *J. Chem. Phys.*, **2**, 58 (1938), have shown that no major changes in structure occur in the abnormal regions but that the expansion behavior is not normal. It should also be noted that Ellefson and Taylor's investigations were carried out on the same samples as were used in the specific heat measurements of Millar[3] and Anderson.[4]

of the Debye function of $\Theta = 176$ and the Einstein function of $\Theta = 206$ was found to fit the data from 53 to 67°K. and was used as the basis of extrapolation. The entropy increment for the region 230 to 260°K. was computed by arbitrarily cutting off the specific heat curves at $C_p = 13.1$ and assigning the remaining energy under the "hump" to the average temperature, 247°K. The corresponding entropy quantity, $(556.5 - 30 \times 13.1)/247 = 0.66$ is included in the item marked "graphical" in Table II. For manganous telluride, the sum of the Debye function of $\Theta = 148$ and the Einstein function of $\Theta = 218$ fits the experimental data from 53 to 67° and was used for the extrapolation.

TABLE II
ENTROPY VALUES

	Mn	MnSe	MnTe
$S_0^{53.1}$ (extrapolation)	0.52	2.78	3.35
$S_{53.1}^{298.1}$ (graphical)	7.09	18.95	19.07
$S_{298.1}$	7.61 ± 0.06	21.7 ± 0.5	22.4 ± 0.5

More error has been allowed in the entropy values for manganese selenide and manganous telluride than normally would be expected, because it was not possible to fit the data over any wide range of temperatures by reasonable Debye and Einstein function combinations on account of the anomalous behavior of these substances. Also in the case of manganous selenide there is an uncertainty of about 0.1 unit involved in connection with the non-reproducibility in the neighborhood of 116°K.

The values for manganous selenide and manganous telluride, when considered with those for manganous oxide and manganous sulfide, are about what would be expected from consideration of the atomic masses involved, provided that account is taken of the deviations of the specific heats at room temperature from the equipartition value.

The entropy figure previously in use for manganese is $S_{298.1} = 7.3 \pm 0.5$,[11] as compared to 7.61 ± 0.06 from this work.

Free Energies at 298.1°K.

Apparently, the only heat of formation value for

(11) Kelley, Bur. of Mines Bull. 394, 1936, 55 pp.

manganous selenide is that of Fabre,[12a] $-21,600$ cal. at room temperature. This value is not sufficiently accurate to warrant any correction for the temperature increment involved in assigning it to 298.1°K.

There appears to be no measurement of the heat of formation of manganous telluride in the literature, and as no other pertinent data exist, it is not possible to compute a free energy of formation value for this substance.

Values for the related compounds, manganous oxide and manganous sulfide, may be obtained based on the heats of formation and entropies. Roth and Müller[12b] found $-96,500$ cal. as the heat of formation of manganous oxide and the writer,[13] after reviewing all the available data, has selected Thomsen's[12a] value for manganous sulfide, $-44,390$.

Table III gives the results of the free energy calculations at 298.1°K. The entropies, other than those of manganese and selenium,[7] are taken from a compilation of the writer.[11]

TABLE III
FREE ENERGIES OF FORMATION AT 298.1°K.

Substance	$\Delta S_{298.1}$	$\Delta H_{298.1}$	$\Delta F°_{298.1}$
MnO	−16.7	−96,500	−91,220
MnS	3.5	−44,390	−45,430
MnSe	3.6	−21,600	−22,670

Summary

Specific heat measurements covering the temperature range 53°K. to room temperature have been made for manganese, manganous selenide, and manganous telluride. The latter two substances behave anomalously.

The following entropy values are given: Mn, $S_{298.1} = 7.61 \pm 0.06$; MnSe, $S_{298.1} = 21.7 \pm 0.5$; and MnTe, $S_{298.1} = 22.4 \pm 0.5$.

Free energy of formation values at 298.1°K. are computed for manganous oxide, manganous sulfide, and manganous selenide.

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(12a) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Vol. II, 1923, p. 1525.
(12b) Second Suppl., Vol. II, 1931, p. 1516.
(13) Kelley, Bur. of Mines Bull. 406, 1937, pp. 154.