(determined by absorption analysis in a Cu(I) solution)[17] was used to saturate the solvent, β,β'-diethoxydiethyl ether, and fill the reaction bulb at 30°. A kinetic run then was carried out in the normal manner except that the buret was filled with pure carbon monoxide and was closed off. By manual operation of the stopcock this carbon monoxide was bled into the reaction bulb frequently so as to replace the carbon monoxide absorbed by the $CH_3Mn(CO)_5$. The composition of the gas and its total pressure in the reaction bulb thus were maintained essentially constant and the consumption of carbon monoxide as a function of time was followed.

(17) W. W. Scott, "Standard Methods of Chemical Analysis," 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., pp. 2349–50.

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Heat Capacities and Thermodynamic Functions of Iron Disulfide (Pyrite), Iron Diselenide, and Nickel Diselenide from 5 to 350°K. The Estimation of Standard Entropies of Transition Metal Chalcogenides[1]

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The heat capacities at low temperatures of purified, natural pyrite and synthetic samples of $FeSe_2$ and $NiSe_2$ were determined by the adiabatic technique. The data on pyrite are in good accord over the common range of measurement with those of Anderson, but not with those of Eucken and Schwers. The values of entropy and the free energy function, $-(F^0 - H_0^0)/T$ at 298.15°K. in cal. g.f.w.$^{-1}$ °K.$^{-1}$ are, respectively: 12.65 and 4.926 for FeS_2; 20.75 and 9.74 for $FeSe_2$; 24.74 and 12.36 for $NiSe_2$. The estimation of the entropies of transition element chalcogenides is discussed.

Introduction

This paper is an integral part of a continuing investigation concerned with the thermophysical properties and phase stabilities of transition element chalcogenides. It deals with three transition element dichalcogenides of which two, iron disulfide and nickel diselenide, possess the pyrite-type structure, and iron diselenide the marcasite-type structure. No heat capacity data are known for iron diselenide or for nickel diselenide, but in two papers[2,3] measurements on pyrite are reported which are in poor agreement with each other over the common range of measurement, and with a third in which enthalpy-type measurements are presented.[4] Another incentive for the redetermination of the heat capacity of pyrite was the marked divergence of pyrite from other substances in the Lindemann[5] relationship as presented by Zemansky[6] in the form $\theta = CT_m^{1/2} \times M^{-1/2}V^{-1/3}$ in which θ is the Debye temperature, C a constant ~200, T_m the melting temperature, M the molecular weight and V the corresponding volume. The further striking departures of the entropies of substances with pyrite-type structure from those of other chalcogenides merit further study.

Experimental

Preparation of the Samples.—Iron disulfide was a pyrite from Bosmo grube, Nordland, Norway. It was crushed to a 30-80 mesh powder and then carefully separated from the accompanying minerals—mostly feldspar—by specific gravity and magnetic methods. Chemical analyses for iron and sulfur by gravimetric methods indicated 46.53 ± 0.03% by weight of iron and 53.45 ± 0.04% of sulfur (theoretical: 46.55% Fe, 53.45% S). Spectrochemical analysis indicated the presence of only the following contaminants (in p.p.m.): Mn (80), Ni (75), and Si (80). X-Ray powder photographs of the sample showed only the presence of lines from pyrite. Its lattice constant is a = 5.416 Å., in close agreement with the value a = 5.4176 Å. determined by Lepp.[7]

Iron diselenide was prepared from high-purity iron and selenium. Merck "Ferrum reductum pro analysi" was reduced with dry purified hydrogen gas at 900° until constant weight was attained. The spectrographic analysis showed as impurities (in p.p.m.): Mn (~10), Ni (~100),

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(1) This work was supported in part by the Division of Research of the United States Atomic Energy Commission, Contract AT(11-1)-70, Project No. 5.

(2) A. Eucken and F. Schwers, *Ber. deut. physik. Ges.*, **14**, 578 (1913).

(3) C. T. Anderson, *J. Am. Chem. Soc.*, **59**, 486 (1937).

(4) R. Ewald, *Ann. Physik*, **44**, 1213 (1914).

(5) A. F. Lindemann, *Physik. Z.*, **11**, 609 (1910).

(6) M. W. Zemansky, "Heat and Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1957, p. 268.

(7) H. Lepp, *Am. Mineralogist*, **41**, 347 (1956).

and Si (~100). The high-purity selenium was analyzed by the Bolidens Gruvaktiebolag and found to contain the following impurities (in p.p.m.): Cl (2), Fe (0.8), K (0.3), Na (0.4), and non-volatile matter (12). A stoichiometric mixture of the elements was heated slowly to 1000° in an evacuated and sealed silica tube, kept there for about two hr., and then cooled to room temperature. The tube was opened in a dry-box filled with nitrogen, and the inhomogeneous product crushed to a gray powder and transferred to a new tube. After being heated at about 340° for one month, the sample was cooled slowly to room temperature during a period of one more month.

X-Ray photographs of the sample showed the presence of the orthorhombic marcasite-type structure reported by Tengnér.[8] The presently determined lattice constants are a = 5.778 Å., b = 4.799 Å., c = 3.583 Å. The agreement with Tengnér's values and more recent ones by Kullerud and Donnay[9] is satisfactory, except that the a-axis reported here is about one per cent. longer.

Nickel diselenide also was prepared from the elements. "Nickel oxide, low in cobalt and iron" from The British Drug Houses, Ltd., was reduced by hydrogen at 500° for five hr. After cooling it was fragmented and heated with hydrogen again, this time at 1000° for four hr. The spectrographic analysis showed the presence of the following impurities (in p.p.m.): Al (100), Ba (1), Ca (10), Co (10), Cr (1), Cu (1), Fe (10), Mg (50), Mn (1), and Si (50). The same selenium was used as for the iron diselenide. The mixture of the elements was heated in an evacuated and sealed silica tube at 800° for one day. Afterwards the temperature was lowered to 400° and kept there for two days. The product then was crushed to a gray powder, transferred to a new tube, and heated for one week at 400°. A small amount of elemental selenium was still visible in the tube; and the temperature was, therefore, increased to 500° for one week. No selenium was then visible, but the sample was nevertheless crushed again, transferred to a new tube, annealed at 300° for one week, and cooled to room temperature over another week. The X-ray photographs showed only the presence of a pyrite-type structure with lattice constant a = 5.9604 Å., in essentially exact agreement with the value obtained earlier[10] for $NiSe_{2.00}$.

Cryostat and Calorimeter.—The Mark I cryostat and the adiabatic method employed are being described elsewhere.[11] The copper calorimeter (laboratory designation W-7) has a capacity of 40.33 cm.^{3} and was used for the measurements on the selenides. This calorimeter has four radial vanes and is gold-plated on all surfaces. Another copper calorimeter (laboratory designation W-9)[12] was used for the measurements on pyrite. The heat capacities of the empty calorimeters were determined in separate series of measurements, in which identical amounts of indium-tin solder for sealing and Apiezon-T grease for thermal contact with the heater and thermometer were used. For pyrite the empty calorimeter represented 40% of the total heat capacity at 5°K., a maximum of 84% at 16°K., and about 30% above 100°K. A more favorable situation obtained for $FeSe_2$ in which the contribution of the heat capacity of the empty calorimeter was about 40% of the total from 5 to 25°K. and decreased gradually to about 30% at 350°K. For $NiSe_2$ the heat capacity of the empty calorimeter was 25 ± 3% of the total over the entire range.

Temperatures were determined with a capsule-type, strain-free, platinum resistance thermometer (laboratory designation A-3) contained within an axial well in each calorimeter. A 150-ohm constantan heater was bifilarly wound on a grooved cylindrical copper sleeve, closely fitted to the resistance thermometer. Apiezon-T grease permitted the ready removal of this heater-thermometer from a calorimeter and hence the interchangeability of calorimeters. The thermometer was calibrated by the U. S. National Bureau of Standards. Temperatures are considered to be in accord with the thermodynamic temperature scale within 0.03°K. from 10 to 90°K. and within 0.04°K. from 90 to 350°K. Temperature increments may of course be determined with more precision than absolute temperatures and probably are correct to a few tenths of a millidegree after correction for quasi-adiabatic drift.

Results and Discussion

The experimental heat capacities are presented in chronological order for the mean temperatures in Table I and graphically in Figure 1. These data have been corrected for the curvature, *i.e.*, for the

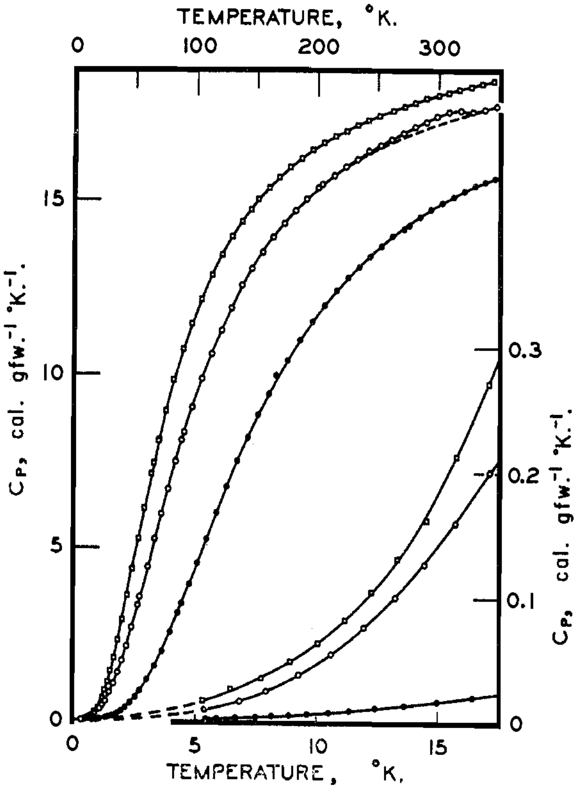

Fig. 1.—Experimental heat capacities of the dichalcogenides on a gram formula weight basis: ● represents FeS_2 (pyrite), ○ represents $FeSe_2$, and □ represents $NiSe_2$.

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[8] S. Tengnér, *Z. anorg. u. allgem. Chem.*, **239**, 126 (1938).

[9] G. Kullerud and G. Donnay, *Geochim. et Cosmochim. Acta*, **15**, 73 (1958).

[10] F. Grønvold and E. Jacobsen, *Acta Chem. Scand.*, **10**, 1440 (1956).

[11] E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

[12] E. Greenberg and E. F. Westrum, Jr., *J. Am. Chem. Soc.*, **78**, 4526 (1956).

difference between the measured $\Delta H/\Delta T$ and the limit as ΔT approaches zero. The approximate values of ΔT used in the determination usually can be estimated from the increment between the adjacent mean temperatures tabulated in Table I. These values are considered to have a probable error less than 5% at 5°K., decreasing to 1% at 10°K., and to less than 0.1% above 25°K., except for FeS_2 where the probable errors are approximately twice as great below 50°K., because of the relatively small heat capacity of this sample.

TABLE I

HEAT CAPACITIES OF IRON AND NICKEL DICHALCOGENIDES

(cal. g.f.w.$^{-1}$ °K.$^{-1}$)

T	C_P
FeS_2 (Pyrite) gram formula weight = 119.98 g.	
Series I	
88.33	3.409
94.32	3.949
101.09	4.572
108.46	5.249
116.55	5.991
125.07	6.740
113.89	7.487
142.51	8.173
151.07	8.818
159.84	9.430
Series II	
4.60	0.0029
5.06	0.0028
5.43	0.0021
5.89	0.0020
6.65	0.0025
7.49	0.0030
8.16	0.0036
8.87	0.0042
9.62	0.0046
10.49	0.0079
11.37	0.0080
12.45	0.0102
13.65	0.0122
14.98	0.0152
16.46	0.0190
18.06	0.0257
19.77	0.0335
21.56	0.0437
23.56	0.0581
25.78	0.0765
28.28	0.1020
31.23	0.1409
34.63	0.1948
38.18	0.2739
41.86	0.3712
45.88	0.5050
50.15	0.6772
53.99	0.8615
59.86	1.187
66.09	1.159
72.30	2.044
79.05	2.591
85.37	3.141
Series III	
165.68	9.953
175.23	10.399
185.37	10.975
195.90	11.520
206.03	11.992
215.79	12.421
225.20	12.791
234.29	13.103
243.43	13.413
252.56	13.705
261.95	13.986
271.37	14.206
275.57	14.308
284.53	14.561
293.71	14.756
302.98	14.963
312.19	15.15
321.44	15.31
330.09	15.47
338.12	15.58
346.11	15.67
$FeSe_2$ gram formula weight = 213.77 g.	
Series I	
53.66	3.567
60.13	4.450
65.85	5.248
71.07	5.944
76.51	6.660
82.66	7.464
89.61	8.304
Series II	
5.36	0.0080
6.81	0.0152
7.91	0.0234
9.24	0.0409
10.59	0.0603
11.96	0.0768
13.23	0.1004
14.47	0.1268
15.74	0.1592
17.15	0.2003
18.81	0.2576
20.80	0.3381
23.12	0.4470
25.80	0.5572
28.81	0.8095
32.05	1.070
35.43	1.379
38.97	1.746
42.73	2.166
47.10	2.703
51.96	3.334
Series III	
87.69	8.071
96.27	9.022
104.45	9.853
112.32	10.582
120.26	11.257
128.67	11.908
137.28	12.553
145.74	13.027
154.32	13.506
163.26	13.953
172.22	14.344
181.34	14.711
190.93	15.053
200.38	15.358
203.92	15.456
213.37	15.720
222.97	15.968
232.35	16.19
241.81	16.42
251.35	16.60
260.79	16.77
270.31	16.95
279.94	17.12
289.43	17.26
298.68	17.44
308.07	17.56
317.67	17.60
327.45	17.58
337.48	17.65
347.46	17.74
$NiSe_2$ gram formula weight = 216.63 g.	
Series I	
64.88	7.427
69.16	8.082
75.04	8.929
81.54	9.815
88.85	10.702
96.10	11.446
103.76	12.141
112.23	12.834
120.73	13.435
129.02	13.957
136.89	14.391
144.63	14.730
152.32	15.10
151.60	15.06
159.52	15.36
167.82	15.67
176.80	15.95
186.18	16.21
195.62	16.45
204.99	16.66
214.17	16.85
223.30	17.01
232.28	17.17
241.27	17.33
250.48	17.46
262.05	17.60
271.20	17.73
280.33	17.83
289.44	17.95
298.50	18.04
307.57	18.12
316.73	18.21
325.99	18.30
335.39	18.38
344.95	18.47
Series II	
5.27	0.016
6.43	0.026
7.69	0.035
8.92	0.053
10.06	0.068
11.20	0.083
12.27	0.1041
13.35	0.1311
14.54	0.1615
15.77	0.2130
17.10	0.2710
18.61	0.3512
20.40	0.4672
22.57	0.6401
24.89	0.8627
27.20	1.119
29.67	1.435
32.48	1.837
35.67	2.332
39.26	2.933
43.29	3.633
47.44	4.383
52.26	5.254
57.17	6.125
62.87	7.098
69.18	8.086

The data on pyrite differ by several per cent. from those reported by Anderson[3] over the range 55 to 70°K. and by less than 0.5% at higher temperatures (*cf.* Figure 2). The deviations from the earlier data of Eucken and Schwers,[2] also shown in Figure 2, are 40% at 22°K. and gradually diminish to about 2% near 80°K. The present data are considered the most reliable both in terms of purity of sample and precision. The integrated enthalpies of this research are larger by 1.5% at 301°K., 0.7% at 235°K., and 0.0% at 138°K. than the enthalpy data of Ewald.[4]

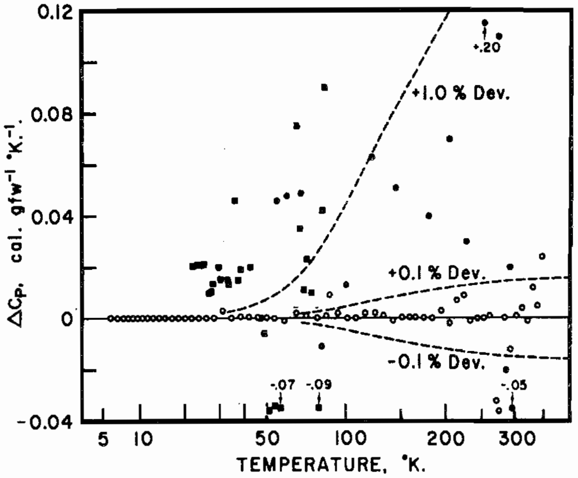

Fig. 2.—Deviation from the smoothed heat capacity curve of pyrite for the actual experimental values of this research (○), of Eucken and Schwers[2] (■), and of Anderson[3] (●).

The thermodynamic functions given in Table II are obtained from the heat capacity data by integration of a least squares fitted curve through the experimental points and numerical quadrature thereof by high-speed digital computers. The thermodynamic functions are considered to have a probable error less than 0.1% above 100°K. The entropy of FeS_2 is in good accord with the value 12.7 ± 0.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$ reported by Anderson.[3]

In $FeSe_2$ a small heat capacity anomaly with a maximum around 310°K. and an entropy increment of about 0.02 cal. g.f.w.$^{-1}$ °K.$^{-1}$ are probably caused by Fe_3Se_4 in the sample. Contamination by this substance is very difficult to avoid and to detect. The Fe_3Se_4 sample has a lambda-type anomaly in the same temperature region[13] with an entropy increment of transition of about 2 cal. g.f.w.$^{-1}$ °K.$^{-1}$. Hence, one mole per cent. of Fe_3Se_4 would be able to cause the anomaly. Assuming strict stoichiometry of the phases, two mole per cent. of selenium also would be present in the sample. The presence of this amount of Fe_3Se_4 and selenium in the sample would increase its observed heat capacity. Thus, the entropy of pure $FeSe_2$

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[13] F. Grønvold and E. F. Westrum, Jr., *Acta Chem. Scand.*, **13**, 241 (1959).

TABLE II

THERMODYNAMIC PROPERTIES OF IRON AND NICKEL DICHALCOGENIDES

T, °K.	C_p cal. g.f.w.$^{-1}$ °K.$^{-1}$	$S° - S_0°$ cal. g.f.w.$^{-1}$ °K.$^{-1}$	$H° - H_0°$ cal. g.f.w.$^{-1}$	$\frac{-(F° - H_0°)}{T}$ cal. g.f.w.$^{-1}$ °K.$^{-1}$
FeS_2 (Pyrite); gram formula weight = 119.98 g.				
5	(0.0015)	(0.0005)	(0.0019)	(0.0001)
10	.0056	.0018	.0139	.0004
15	.0151	.0058	.0642	.0015
20	.0348	.0124	.1832	.0032
25	.0735	.0239	.4406	.0062
30	.1230	.0408	.9098	.0104
35	.2044	.0654	1.716	.0164
40	.3196	.0999	3.010	.0246
45	.4739	.1460	4.977	.0354
50	.6705	.2057	7.820	.0493
60	1.193	.3716	17.00	.0883
70	1.874	.6049	32.22	.1446
80	2.675	.9063	54.88	.2203
90	3.554	1.272	85.98	.3163
100	4.471	1.693	126.1	.4324
110	5.394	2.163	175.4	.5681
120	6.297	2.671	233.9	.7219
130	7.163	3.210	301.2	.8924
140	7.979	3.771	377.0	1.078
150	8.738	4.347	460.6	1.277
160	9.440	4.934	551.6	1.487
170	10.08	5.526	649.2	1.707
180	10.68	6.119	753.1	1.936
190	11.22	6.711	862.6	2.171
200	11.72	7.300	977.3	2.413
210	12.17	7.883	1096.8	2.660
220	12.58	8.459	1220.6	2.910
230	12.96	9.026	1348.4	3.164
240	13.31	9.585	1479.7	3.420
250	13.63	10.135	1614.4	3.677
260	13.92	10.675	1752.2	3.936
270	14.20	11.206	1892.8	4.196
280	14.45	11.727	2036.1	4.455
290	14.68	12.238	2181.8	4.715
300	14.90	12.740	2329.7	4.974
350	15.66	15.11	3097.3	6.255
273.15	14.28	11.37	1937	4.277
298.15	14.86	12.65	2302	4.926
$FeSe_2$; gram formula weight = 213.77 g.				
5	(0.007)	(0.002)	(0.009)	(0.001)
10	.047	.016	.117	.004
15	.139	.050	.560	.013
20	.307	.111	1.64	.029
25	.537	.204	3.73	.055
30	.892	.330	7.24	.089
35	1.335	.501	12.79	.135
40	1.860	.713	20.75	.194
45	2.446	.965	31.50	.265
50	3.078	1.255	45.29	.349
60	4.428	1.934	82.75	.555
70	5.808	2.721	133.9	.807
80	7.128	3.583	198.7	1.100
90	8.334	4.494	276.1	1.426
100	9.412	5.429	365.0	1.779
110	10.38	6.372	464.0	2.154
120	11.24	7.313	572.2	2.545
130	12.01	8.244	688.5	2.947
140	12.69	9.159	812.1	3.359
150	13.28	10.056	942.1	3.775
160	13.80	10.930	1077.6	4.195
170	14.25	11.780	1217.8	4.617
180	14.66	12.607	1362.4	5.038
190	15.02	13.409	1510.8	5.457
200	15.34	14.188	1662.7	5.874
210	15.63	14.944	1817.6	6.288
220	15.89	15.677	1975.3	6.698
230	16.13	16.389	2135.4	7.104
240	16.36	17.080	2297.9	7.506
250	16.58	17.753	2462.6	7.902
260	16.77	18.407	2629.3	8.294
270	16.94	19.043	2797.9	8.680
280	17.11	19.662	2968.1	9.061
290	17.28	20.265	3140.0	9.437
300	17.45	20.854	3313.7	9.808
350	17.60	23.568	4194.3	11.584
273.15	16.99	19.24	2851	8.80
298.15	17.42	20.75	3281	9.74
$NiSe_2$; gram formula weight = 216.63 g.				
5	(0.015)	(0.005)	(0.019)	(0.001)
10	.063	.027	.194	.006
15	.181	.072	.760	.021
20	.440	.155	2.24	.044
25	.873	.297	5.46	.079
30	1.481	.508	11.28	.132
35	2.226	.790	20.50	.205
40	3.059	1.141	33.67	.299
45	3.944	1.552	51.17	.415
50	4.847	2.014	73.14	.551
60	6.610	3.055	130.51	.880
70	8.213	4.197	204.80	1.272
80	9.620	5.388	294.14	1.711
90	10.81	6.592	396.42	2.187
100	11.81	7.784	509.7	2.687
110	12.66	8.951	632.2	3.204
120	13.39	10.085	762.6	3.730
130	14.01	11.182	899.7	4.261
140	14.55	12.240	1042.5	4.794
150	15.00	13.260	1190.3	5.324
160	15.40	14.241	1342.4	5.851
170	15.74	15.185	1498.1	6.373
180	16.05	16.093	1657.0	6.888
190	16.31	16.968	1818.8	7.395
200	16.55	17.811	1983.2	7.895
210	16.77	18.624	2149.8	8.387
220	16.97	19.409	2318.5	8.870
230	17.15	20.167	2489.1	9.345
240	17.31	20.900	2661.3	9.811
250	17.45	21.609	2835.1	10.629
260	17.58	22.296	3010.3	10.718
270	17.71	22.962	3186.8	11.160
280	17.83	23.609	3364.4	11.593
290	17.95	24.237	3543.4	12.018
300	18.06	24.847	3723.4	12.435
350	18.51	27.665	4637.8	14.414
273.15	17.75	23.17	3242	11.30
298.15	18.04	24.74	3690	12.36

may be lower than reported here by about 0.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$.

The comparatively small differences between the present heat capacity data for pyrite and the best earlier values[3] leaves pyrite as an outstanding exception to the Lindemann[5] relationship with a value of C equal to about 200 for many nonmetals and compounds according to Zemansky.[6] In Table III are compiled data for the three dichalcogenides studied here, which show that the value of the constant C is even higher for $FeSe_2$ than for pyrite. The melting temperature of pyrite is taken from Kullerud and Yoder,[14] that of $FeSe_2$ is from a personal communication from Kullerud, and that of $NiSe_2$ from unpublished work at the University of Oslo. The densities have been calculated from the X-ray data, assuming fully occupied lattice positions, and the θ values calculated from the C_p values at 50°K. Some reservation must be made, however, when applying the Lindemann relationship to compounds in question, since pyrite (and possibly the other substances also) undergoes peritectic rather than congruent melting at the temperature indicated. Even so, marked deviations from the relationship are observed for all three compounds, and the outstanding property of pyrite is its high θ value or exceptionally low heat capacity at low temperatures.

TABLE III

LINDEMANN-ZEMANSKY RELATIONSHIPS FOR THE DICHALCOGENIDES

Solid	T_m, °K.	M, g. mole^{-1}	g. cm.$^{-3}$	$\left(\frac{T_m}{MV^{2/3}}\right)^{1/2}$	θ	C
FeS_2	1016	119.98	5.01	1.00	637	637
$FeSe_2$	622	213.77	7.05	0.57	366	642
$NiSe_2$	~900	216.63	6.72	0.64	297	464

Estimation of Entropies of Transition Element Chalcogenides.—Despite the high current interest in the chalcogenides, it is unlikely that either low temperature heat capacity data or equilibrium data permitting direct calculation of their entropies will be available in the near future because of the considerable endeavor involved in the preparation of pure samples and the study of their thermophysical properties. It therefore seems desirable to find a basis for estimating their entropies with a reasonable degree of accuracy. A general approach to this problem was sought by Latimer,[15] who formulated the entropy of an element in a compound in terms of the atomic weight (A) as

$$S_{298} = 3/2\ R \ln A + S'$$

The value of S' was evaluated as -0.94 by means of the standard entropy of NaCl, one of the most accurately determined entropies at that time. Eastman[16] showed that the value of the constant S' varied for different salts and suggested that it be replaced by the term $k \log M$, in which M was the molecular weight of the compound and k an empirical constant.

Latimer's success in assuming the entropy of a compound to be the sum of the entropy contributions of the elements involved, and thus proportional to the logarithm of the product of their atomic weights, led Wenner[17] to assume the entropy to be proportional to the logarithm of the molecular weight of the compound according to the equation

$$S_{298} = a \log M + b$$

in which a and b are empirical constants for the group of compounds considered. Treadwell and Mauderli[18] proposed, more in accordance with the relation of Latimer, the equation

$$S_{298} = c\ (\log A_c + d \log A_a) + e$$

in which A_c and A_a are the atomic masses of cation and anion, respectively, c and e are characteristic constants for homologous salt series, and d is a constant numerically equal to the oxidation number of the cation. Such restricted schemes naturally have better chances of success than a more general one neglecting characteristic properties of the group of compounds in question. Latimer's[19] empirically adjusted entropy *versus* atomic weight relationship, leading to a relative decrease in entropy for elements with atomic weight less than 150 and an increase for the heavier ones, has improved on the usefulness of his method. Drozin[20] has attempted to show that the entropy of some sulfides of monovalent and bivalent metals can be accounted for by the formula

$$S = f + gN$$

where N is the number of neutrons in the "molecule" and f and g are constants.

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Kireev[21] in discussing new ways of estimating thermodynamic properties observed that "the atomic entropy of formation," *i.e.*, the entropy of a given compound minus that for the gaseous monatomic elements in question, under specified conditions, is a quantity primarily dependent upon the number of atoms in the molecule. A comparison for compounds of the same type revealed regularities that were used[22] in calculating missing entropy values for some chalcogenides.

Other schemes, based upon correlation of data, also have been suggested. Kelley,[23] for example, in attempting to find usable relationships for the entropy of oxides formulated the empirical equation

$$S°_{298} = 3/2\ R\ x \ln A_e + 3/2\ R\ y\ r \ln 16 + (x + y)\ S''$$

in which A_e is the atomic weight of the metal in the compound Me_xO_y, and r and S'' are constants. The r is defined as $(C_p - 6x)/6y$ (in which C_p is the molal heat capacity of the compound at 298°K.) and thus represents the fractional oxygen equipartition heat capacity. S'' was taken as -3.5 for oxides of the types MeO and MeO_2, and as -3.1 for those of the types Me_2O_3, Me_2O_4, Me_2O_5, and Me_3O_4. The largest discrepancies were noted for the oxides of manganese, iron, and copper, amounting to 6.7 cal. $mole^{-1}$ $°K.^{-1}$ for Fe_2O_3. For sulfides a similar equation did not meet with equal success.

Entropy values for ions in inorganic salts, based on the additivity principle, were deduced by Gapon.[24] Considerable disagreement between values calculated by his method and existing experimental data, noted by Yatsimirskii,[25] led Gapon[26] to revise the ionic entropy values. Regular interpolation or extrapolation of entropies for homologous compounds has been shown by Drozin[27] to give favorable results when applied to metal oxides, halides, etc. Karapet'yants[28] assumed that the entropies of related compounds were a linear function of the heat capacities at 298°K., while Turkdogan[29] obtained nearly linear relationships between the entropies of sets of compounds, such as the oxides and sulfides of several elements. Such methods are limited, however, by the availability of data. A general discussion of the relationships between entropy and heat capacity was given by Strelkov[30] in light of the corresponding states concept and the applicability shown to be better the higher the molecular weight, molal volume, and critical temperature of the compound in question.

None of the schemes proposed takes fully into consideration the effects of unpaired electrons, and therefore is unable to account for characteristic differences observed for transition metal compounds. Moreover, the scheme proposed by Latimer,[19] for example, apparently would ascribe the same entropy to MeS_2 compounds irrespective of whether they contained S^{2-} or S_2^{2-} ions. In the following, concern is restricted to transition element chalcogenides, starting with those for which the magnetic contributions are negligible (at least as a first approximation), and subsequently including those with larger magnetic contributions. The entropy contributions of conduction electrons are not considered in detail, nor are structural order–disorder transitions. If such transitions occurred below the reference temperature, they would have complicated the entropy estimation considerably.

Experimentally determined entropy values for transition metal chalcogenides are collected in Table IV. Most of them have been derived from low temperature heat capacity measurements. In some cases (indicated by the symbol *e* in front of the entropy value) data from high temperature heterogeneous equilibria have been taken into account, either because of lack of more precise data from heat-capacity measurements, or because of the interest in comparing entropies by different methods in which zero-point entropy may be involved. In some instances entropy values had to be evaluated from equilibrium data in the literature. Such values are marked by an asterisk and details about the entropy estimates are found in the Appendix.

A striking feature of the collected data is the relatively small influence of mass on the entropy at 298.15°K. for many homologous compounds: TiO_2, ZrO_2, HfO_2, ThO_2 [12.01, 12.12, 14.18, 15.59]; $VO_{2.5}$, $NbO_{2.5}$, $TaO_{2.5}$ [15.65, 16.4, 17.1]; $NiTe_{1.1}$, PdTe, PtTe [20.09, 21.42, 19.41]; $NiTe_2$, $PdTe_2$, $PtTe_2$ [28.76, 30.25, 28.92]: FeS_2, RuS_2, OsS_2 [12.65, 10.4, 13.1]. This is apparently no

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TABLE IV

ENTROPIES OF BINARY, SOLID, TRANSITION ELEMENT CHALCOGENIDES AT 298.15°K.[a]

In cal. g.f.w.$^{-1}$ °K.$^{-1}$

$YO_{1.5}$	c	11.85^{31}
$LaO_{1.5}$	h	15.29^{31}
CeO_2	c	14.89^{32}
CeS	c	18.7^{33}
$CeS_{1.5}$	c	21.5^{33}
$LuO_{1.5}$	c	$13.^{34}$
$TiO_{0.33}$	-	6.87^{35}
TiO	c	8.31^{36}
$TiO_{1.5}$	h	9.42^{36}
$TiO_{1.67}$	m	10.31^{36}
TiO_2	ru	12.01^{37}
TiO_2	an	11.93^{37}
TiS_2	h	18.73^{38}
ZrO_2	c	12.12^{39}
HfO_2	c	14.18^{40}
ThO_2	c	15.59^{41}
ThS_2	o	23.0^{33}
VO	c	9.31^{42}
$VO_{1.5}$	r	11.75^{43}
VO_2	m	12.25^{43}
$VO_{2.17}$	m	$e14.5^{*}$
$VO_{2.5}$	r	15.65^{43}
NbO_2	t	13.03^{44}
$NbO_{2.5}$	H	16.4^{45}
$TaO_{2.5}$	L	17.1^{46}
$CrO_{1.5}$	r	9.7^{47}
MoO_2	m	11.06^{44}
MoO_3	o	18.58^{48}
$MoS_{1.5}$	t	$e15.7^{*}$
MoS_2	h	14.96^{49}
WO_2	t	12.08^{50} $e17.1^{51}$
$WO_{2.72}$	m	$e15.0^{52}$ $e25.0^{53}$
$WO_{2.90}$	m	$e23.6^{53}$
$\alpha\text{-}WO_3$	m	18.15^{50} 19.90^{54}
$\beta\text{-}WO_3$	t	$e17.7^{55}$
WS_2	h	$e22.7^{56}$
UO_2	c	18.63^{57}
$UO_{2.25}$	c	20.07^{58}
$\alpha\text{-}UO_{2.33}$	t	19.73^{59}
$\beta\text{-}UO_{2.33}$	t	19.96^{59}
$UO_{2.67}$	o	22.51^{60}
$\alpha\text{-}UO_3$	h	23.57^{57}
MnO	c	14.27^{42}
$MnO_{1.33}$	t	11.83^{61}
$\alpha\text{-}MnO_{1.5}$	c	13.2^{45}
$\beta\text{-}MnO_2$	t	12.68^{62}
α-MnS	c	18.7^{63}
MnSe	c	21.7^{64}
MnTe	h	22.4^{64}
$ReO_{3.5}$	h	24.77^{65}
ReS_2	-	$e13.9^{*}$
$FeO_{1.05}$	c	15.1^{42} $e14.4^{66}$
$FeO_{1.33}$	c	12.01^{67}
$\alpha\text{-}FeO_{1.5}$	r	10.44^{68}
FeS	h	14.42^{69}
$FeS_{1.14}$	h	16.57^{69}
FeS_2	c	12.65
$FeSe_{0.96}$	t	16.53^{13}
$FeSe_{1.14}$	h	20.96^{13}
$FeSe_{1.33}$	m	22.29^{13}
$FeSe_2$	o	20.76
$FeTe_{0.9}$	t	19.16^{70}
$FeTe_2$	o	23.94^{70}
RuS_2	c	$e12.5^{56}$ $e10.4^{71}$
OsO_4	(wh)	$e29.7^{72}$
OsO_4	(yel)	$e34.7^{73}$
OsS_2	c	$e13.1^{71}$
CoO	c	12.66^{74} $e11.94^{75}$
$CoO_{1.33}$	c	8.17^{74}
$CoS_{0.89}$	c	$e13.1^{*}$
CoS	h	$e15.2^{*}$
$CoS_{1.33}$	c	$e15.6^{*}$
CoS_2	c	$e13.7^{*}$
$RhO_{1.5}$	r	$e\ 9.2^{*}$
IrO_2	t	$e14.6^{*}$
$IrS_{1.5}$	—	$e11.6^{71}$
IrS_2	o	$e14.7^{71}$
NiO	c	9.08^{74} $e\ 8.93^{76}$
$NiS_{0.67}$	r	$e11.1^{*}$
NiS	r	$e14.8^{*}$
NiS	h	$e15.8^{*}$
NiS_2	c	$e18.5^{*}$
$NiSe_{1.05}$	h	17.97^{77}
$NiSe_{1.14}$	o	18.44^{77}
$NiSe_{1.25}$	m	19.14^{77}
$NiSe_2$	c	24.74
$NiTe_{1.1}$	h	20.09^{78}
$NiTe_{1.5}$	h	23.99^{78}
$NiTe_2$	h	28.76^{78}
PdO	t	$e\ 9.7^{*}$
PdTe	h	21.42^{79}
$PdTe_2$	h	30.25^{71}
PtS	t	13.17^{79}
PtS_2	h	17.85^{71}
PtTe	o	19.41^{79}
$PtTe_2$	h	28.92^{71}
$CuO_{0.5}$	c	11.22^{80}
CuO	m	10.19^{81}
$CuS_{0.5}$	o	14.45^{82} $e14.25^{83}$
CuS	h	15.9^{82}
$AgO_{0.5}$	c	14.55^{84}
$AgS_{0.5}$	o	17.07^{85} $e16.8^{86}$
$AgSe_{0.5}$	-	17.88^{85}
$AgTe_{0.53}$	o	18.72^{85}
ZnO	h	10.43^{87}
ZnS	h	13.8^{87}
ZnTe	c	$e18.9^{88}$
CdO	c	13.1^{89}
CdS	h	17^{87}
CdTe	c	$e22.2^{88}$
HgO	o	16.77^{90}
HgO	r	$e17.3^{87}$

[a] Symbols represent following structures: an, anatase; c, cubic; h, hexagonal; H, high temperature polymorph; L, low temperature polymorph; m, monoclinic; o, orthorhombic; r, rhombohedral; ru, rutile; t, tetragonal. An *e* indicates values from heterogeneous equilibrium data; an asterisk (*) indicates values evaluated here (*cf.* Appendix). Superscripts indicate references.

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longer the case in the beginning and end of the transition periods: $YO_{1.5}$, $LaO_{1.5}$ [11.65, 15.29]; ZnO, CdO, HgO [10.43, 13.1, 16.6], nor for the heaviest elements of the groups, *i.e.*, the actinides.

For a more detailed analysis it is profitable to assign, as Latimer did, all variation in entropy for various compounds of a metal to the anion present. Recommended cationic entropy contributions are presented in Table V. The most striking departure from Latimer's scheme[19] is the constant value of 10.5 cal. g. atom^{-1} °K.$^{-1}$ for the mid-portions of the transition series. Values intermediate betweeen 10.5 and those of Latimer (except for copper and silver) were adopted at the periphery of this region. Where identical values were adopted, the number has been italicized.

The comparison for the sulfides, selenides, and tellurides will be considered apart from that of the oxides. Strongly paramagnetic and ferromagnetic compounds also are discussed separately. Furthermore, certain structural differences require special assumptions about the entropy contribution from the anion.

Sulfides, Selenides, and Tellurides Not Containing X_2^{2-}-Groups.—If the anionic entropy contribution is taken to be proportional to the X/Me atomic ratio, rather good agreement for compounds with small effective magnetic moments is obtained using the values in Table VI.

Entropies estimated by combining the values from Tables V and VI are listed in Table VII, together with the differences between estimated and observed values. The mean deviation over all values (except that for WS_2, which is probably erroneous) is only 1.4 cal. g.f.w.$^{-1}$ °K.$^{-1}$, or 7.8%, while for Latimer's values, where applicable, it would have amounted to 2.5 cal. g.f.w.$^{-1}$ °K.$^{-1}$, or 14.0%. The discrepancies from his scheme are especially striking for the compounds PtS and PtTe (7.0 and 7.9 cal. g.f.w.$^{-1}$ °K.$^{-1}$, respectively).

In Table VII only compounds with relatively small magnetic moments are included. The presence of unfilled 3d, 4f, and 5f shells, and in decreasing incidence 4d, 5d, and 6d shells, with varying number of closely spaced energy levels, introduces other significant entropy terms. In addition to the changing population of the quantum levels associated with the magnetic system of a single atom, the contribution from coöperative phenomena such as ordering of spins and distribution of electrical charges also must be taken into account.

For most of the compounds discussed here the orbital magnetic contribution is quenched and the entropy difference between equipartition of the spins among the possible states and complete ordering of them is $\Delta S = R \ln (2S + 1)$, where S is the spin quantum number. Since some order apparently is present in all compounds at 298°K. (even in those containing Mn^{2+} ions), the effective

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TABLE V

ESTIMATED CATIONIC ENTROPY CONTRIBUTIONS IN SOLID TRANSITION METAL CHALCOGENIDES

In cal. g. atom^{-1} °K.$^{-1}$ at 298°K.; values identical with those of Latimer[19] are in *italics*.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
9.7	10.5	10.5	10.5	10.5	10.5	10.5	*10.5*	12.0	*10.9*
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
12.0	10.5	10.5	10.5	10.5	10.5	10.5	10.5	14.0	*12.9*
La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
13.8	12	11	10.5	10.5	10.5	10.5	10.5	*15.3*	*15.4*
Ac	Th	Pa	U						
16	15	15	15						

TABLE VI

ANIONIC ENTROPY CONTRIBUTIONS IN SOLID TRANSITION METAL CHALCOGENIDES

In cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 298°K.

S	Se	Te	[S_2]	[Se_2]	[Te_2]
3.0	7.0	9.5	3.0	10.0	13.5
$0_{0.33}$	$0_{0.5}$	0	$0_{1.33}$	$0_{1.5}$	$0_{1.67}$
(−2.5)	−2	−2	−1	0	+1
0_2	$0_{2.25}$	$0_{2.5}$	0_3	$0_{3.5}$	0_4
+2	+3	+6	+8	(+14)	(+20)

TABLE VII

ESTIMATED ENTROPIES FOR SULFIDES,[a] SELENIDES,[a] AND TELLURIDES[a]

Comp.	$S°_{est}$	$S°_{obs} - S°_{est}$	Comp.	$S°_{est}$	$S°_{obs} - S°_{est}$
TiS_2	16.5	+2.2	$PdTe_2$	29.5	+0.8
ThS_2	21	+2.0	PtS	13.5	−0.3
$MoS_{1.5}$	15.0	*e*+0.7	PtS_2	16.5	+1.4
MoS_2	16.5	−1.5	PtTe	20.0	−0.6
WS_2	16.5	(*e*+6.2)	$PtTe_2$	29.5	−0.6
ReS_2	16.5	*e*−2.6	$CuS_{0.5}$	13.5	+1.0
$CoS_{0.89}$	13.2	*e*−0.1			*e*+0.8
$IrS_{1.5}$	15.0	*e*−3.4	CuS	15.0	+0.9
NiS(rh)	13.2	*e*+1.6	$AgS_{0.5}$	15.5	+1.6
NiS(h)	13.2	*e*+2.6			*e*+1.3
$NiSe_{1.05}$	17.9	+0.1	$AgSe_{0.5}$	17.5	+0.4
$NiSe_{1.14}$	18.5	−0.1	$AgTe_{0.53}$	18.8	−0.1
$NiSe_{1.25}$	19.2	−0.1	ZnS	13.9	−0.1
$NiTe_{1.1}$	21.0	−0.9	ZnTe	20.0	*e*−1.1
$NiTe_{1.5}$	24.8	−0.8	CdS	15.9	+1.1
$NiTe_2$	29.5	−0.7	CdTe	22.4	*e*−0.2
PdTe	20.0	+1.2			

[a] Exclusive of those containing X_2^{2-}-groups.

magnetic moment as calculated from the expression $\mu_{eff} = 2.83 (\chi_{mol} T)^{1/2} \mu_B$ has been used as a measure of the degree of disorder attained at this temperature. In the zeroth approximation, $\mu_{eff} = 1.73\ \mu_B$ is interpreted as an entropy acquisition of $R \ln 2$, or 1.38 cal. g.f.w.$^{-1}$ °K.$^{-1}$, $\mu_{eff} = 2.83\ \mu_B$ as an entropy acquisition of $R \ln 3$, etc.

In Table VIII the magnetic entropy, estimated from the effective magnetic moment, has been added to the lattice contribution to give S_{est}. This decreases the mean deviation to 5%, or less than half of what it would have been if the magnetic entropy had not been taken into account. The discordance noted for α-MnS is probably occasioned by the more ionic character of this sulfide (than that of FeS, for example), and the corresponding increase in the interatomic distances and alteration in the vibrational spectrum give rise to a more rapid increase in heat capacity at low temperatures.

TABLE VIII

ESTIMATED ENTROPIES FOR MAGNETIC SULFIDES,[a] SELENIDES,[a] AND TELLURIDES[a]

Comp.	μ_{eff}	S_{magn}	$S°_{est}$	$S°_{obs} - S°_{est}$
CeS	2.2[91]	1.8	18.6	+0.1
$CeS_{1.5}$	2.5[92]	2.0	20.3	+1.2
α-MnS	3.6[93]	2.6	16.1	+2.6
MnSe	4.0[93]	2.8	20.3	+1.4
MnTe	2.9[93]	2.2	22.2	+0.2
FeS	1.6[94]	1.3	14.8	−0.4
$FeS_{1.14}$	f[b94]	(1.5)	16.0	+0.6
$FeSe_{0.96}$	?	?	17.2	−0.7
$FeSe_{1.14}$	f[95]	(1.5)	20.0	+1.0
$FeSe_{1.35}$	f[95]	(1.5)	21.3	+1.0
$FeTe_{0.9}$	1.7[96]	1.4	20.5	−1.3
CoS	0.8[97]	0.5	14.0	*e*+1.2
$CoS_{1.33}$	1.4[98]	0.8	15.3	*e*+0.3
$NiS_{0.67}$	1.0[99]	0.7	13.2	*e*−2.2

[a] Only those not containing X_2^{2-}-groups and with effective magnetic moments higher than 0.8 Bohr magneton at 298°K. are considered. [b] f denotes ferrimagnetism.

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Sulfides, Selenides, and Tellurides Containing X_2^{2-}-Groups.—Analysis of the available data on disulfides (excluding NiS_2) apparently indicates that the X_2^{2-}-group for compounds with pyrite- and marcasite-like structures cannot be attributed as much entropy as two X^{2-}-ions. This finds further support in the rather low entropy values for $FeSe_2$ and $FeTe_2$, and leads to a suggestion of the entropy contributions listed in Table VI. Table IX includes estimates both for essentially non-magnetic compounds, like pyrite and the noble metal disulfides, and those with considerable magnetic contribution to the entropy. The entropies of NiS_2 and $NiSe_2$ are considerably higher than suggested by the present scheme. These compounds are, however, hyperelectronic, show metallic conductance, and also larger interatomic distances because of the presence of more loosely bonded electrons. Thus, additional entropy contributions may be anticipated.

TABLE IX

ESTIMATED ENTROPIES FOR SULFIDES, SELENIDES, AND TELLURIDES CONTAINING X_2^{2-}-GROUPS

Comp.	μ_{eff}	S_{magn}	$S°_{est}$	$S°_{obs} - S°_{est}$
FeS_2	...	...	13.5	−0.8
$FeSe_2$	...	...	20.5	+0.3
$FeTe_2$	0.8[100]	0.5	24.5	−0.6
RuS_2	...	...	13.5	$\begin{cases} e-1.0 \\ e-3.1 \end{cases}$
OsS_2	...	...	13.5	$e-0.4$
CoS_2	2.9[101]	2.2	15.7	$e-2.0$
IrS_2	...	...	13.5	$e+1.2$
NiS_2	1.3[101]	1.0	14.5	$e+4.0$
$NiSe_2$	0.8[10]	0.5	21.0	+3.7

Oxides.—The oxides present a somewhat more complicated picture in that the apparent oxygen contribution to the entropies of different oxides of a metal varies markedly with the O/Me ratio. This is a consequence of the fact that the heat capacities of oxygen-rich oxides in general are much closer to the equipartition value of 6 cal. g. atom.$^{-1}$ °K.$^{-1}$ at 298°K. than the metal-rich ones, so that the constraints are neither negligible nor the same for oxides of different compositions. Assuming the entropy contribution of the metal to be constant, the best agreement is obtained using the entropy values for oxygen given in Table VI.

A comparison of observed and estimated entropies for oxides in which the magnetic entropy contributions are considered negligible is found in Table X. In general the agreement is satisfactory, but it seems as if the present scheme underestimates the entropy contribution for the metals in the first and the two last columns of Table V. Excluding values for three tungsten oxides (for which the experimental data probably are in serious error) the mean deviation of the estimated values from the observed ones is 8.4%.

TABLE X

ESTIMATED ENTROPIES FOR NON-MAGNETIC OXIDES[a]

Comp.	$S°_{est}$	$S°_{obs} - S°_{est}$	Comp.	$S°_{est}$	$S°_{obs} - S°_{est}$
$YO_{1.5}$	10.5	+1.4	WO_2	12.5	$\begin{cases} -0.4 \\ (e+4.6) \end{cases}$
$LaO_{1.5}$	13.8	+1.5			
CeO_2	15.8	−0.9	$WO_{2.72}$	17.5	$\begin{cases} e-2.5 \\ (e+7.5) \end{cases}$
$LuO_{1.5}$	13.8	−0.8			
$TiO_{0.33}$	(8.0)	...	$WO_{2.90}$	18.2	$(e+5.4)$
TiO	8.5	−0.2	α-WO_3	18.5	$\begin{cases} -0.3 \\ +1.4 \end{cases}$
$TiO_{1.5}$	10.5	−1.1			
$TiO_{1.67}$	11.5	−1.2	β-WO_3	18.5	−0.8
TiO_2(ru)	12.5	−0.5	α-UO_3	23	+0.6
TiO_2(an)	12.5	−0.6	$ReO_{3.5}$	(24.5)	...
ZrO_2	12.5	−0.4	OsO_4	(30.5)	...
HfO_2	14.0	+0.2	$RhO_{1.5}$	10.5	$e-1.3$
ThO_2	17.0	−1.4	IrO_2	12.5	$e+2.1$
VO_2	12.5	−0.2	PdO	8.5	$e+1.2$
$VO_{2.5}$	16.5	−0.8	$CuO_{0.5}$	10.0	+1.2
NbO_2	12.5	+0.5	$AgO_{0.5}$	12.6	+2.6
$NbO_{2.5}$	16.5	−0.1	ZnO	8.9	+1.5
$TaO_{2.5}$	16.5	+0.6	CdO	10.9	+2.2
MoO_2	12.5	−1.4	HgO(o)	13.4	+3.4
MoO_3	18.5	+0.1	HgO(r)	13.4	$e+3.9$

[a] Only those with effective magnetic moments less than 0.8 Bohr magneton at 298°K. are considered.

For magnetic oxides the additional entropy contribution has been evaluated in the same way as for the other chalcogenides on the basis of available data for their magnetic susceptibilities. The results are presented in Table XI. In most cases (except for VO, $UO_{2.25}$, β-$UO_{2.33}$, $MnO_{1.33}$, $FeO_{1.5}$, $CoO_{1.33}$, and NiO) λ-type transitions have been observed below 298°K. The entropies directly associated with the peaks are in general considerably smaller than the calculated spin-only contributions, which indicates that the order–disorder process takes place over a rather large temperature range. This phenomenon has been analyzed in detail by Hofmann, *et al.*,[102] for some of the oxides listed in Table XI, and their heat capacities have been resolved into components of lattice and electronic origin.

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TABLE XI

ESTIMATED ENTROPIES FOR MAGNETIC OXIDES

Comp.	μ_{eff}	S_{magn}	$S°_{est}$	$S°_{obs} - S°_{est}$
VO	2.7[103]	2.1	10.6	−1.3
$VO_{1.5}$	1.6[104]	1.3	11.8	0.0
$VO_{2.17}$	1.3[104]	1.0	14.0	+0.5
$CrO_{1.5}$	2.2[105]	1.8	12.3	−2.6
UO_2	2.4[106]	1.9	18.9	−0.3
$UO_{2.25}$	~2.0[106]	1.7	19.7	+0.4
α-$UO_{2.33}$	~1.8[106]	1.5	20.5	−0.8
β-$UO_{2.33}$	~1.8[106]	1.5	20.5	−0.5
$UO_{2.67}$	1.2[106]	0.7	22.7	−0.2
MnO	3.4[107]	2.5	11.0	+3.7
$MnO_{1.33}$	3.1[107]	2.3	11.8	0.0
α-$MnO_{1.5}$	4.1[108]	2.8	13.3	−0.1
β-MnO_2	2.4[107]	1.9	14.4	−1.7
$FeO_{1.05}$	4.1[109]	2.8	11.0	+4.1 *e*+3.4
$FeO_{1.33}$	f[a,110]	(1.5)	11.4[b]	+0.6
α-$FeO_{1.5}$	2.0[111]	1.5	12.0	−1.6
CoO	3.6[112]	2.6	11.1	+1.6 *e*+0.8
$CoO_{1.33}$	1.4[113]	0.8	10.3	−2.1
NiO	1.3[114]	0.8	9.0	+0.1 *e*−0.1
CuO	0.8[115]	0.5	9.3	+0.9

[a] f denotes ferrimagnetism. [b] Electronic contribution added with 0.4 cal. g.f.w.$^{-1}$ °K.$^{-1}$.

In cases where high degrees of magnetic ordering persist at room temperature, as evidenced by the presence of antiferromagnetism or of ferrimagnetism, the entropy estimates may be too high. Such tendencies appear for $CrO_{1.5}$ and α-$FeO_{1.5}$, but not for $FeO_{1.33}$. In the last case, however, an additional order–disorder process is encountered in the changing distribution of ionic charges on the iron atoms for which the entropy increment apparently only amounts to 0.4 cal. g.f.w.$^{-1}$ °K.$^{-1}$. Thus, the magnetic entropy might be overestimated and the charge distribution entropy underestimated. The discrepancies noted for MnO and $FeO_{1.5}$ and some other chalcogenides merit further study.

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Appendix

Entropy data from heterogeneous equilibrium studies have been reëvaluated either with the use of better heat capacity data for the components involved or, in some instances, also by adjusting the reactions to conform with newer concepts about the composition of the phases present. Where possible, the equations for the thermodynamic functions have been used in the form

$$\Delta C_p = -a - 2b \times 10^{-3}T - 2c \times 10^5 T^{-2}$$
$$\Delta H° = \Delta H_0 - aT - b \times 10^{-3}T^2 + 2c \times 10^5 T^{-1}$$
$$\Delta F° = \Delta H_0 + aT \ln T + b \times 10^{-3}T^2 + c \times 10^5 T^{-1} + IT$$
$$\Delta S° = -a - a \ln T - 2b \times 10^{-3}T + c \times 10^5 T^{-2} - I$$

where *a*, *b*, and *c* are known or estimated constants, ΔH_0 and I integration constants, and T the temperature in °K. The values of the integration constants have been determined by combining the equilibrium data in the form

$$\Delta F° = -RT \ln K$$

where R is the gas constant, 1.986 cal. °K.$^{-1}$ mole^{-1}, and K the equilibrium constant, to give the equation

$$(\Delta H_0/T) + I = -4.57 \log K - 2.30\, a \log T - b \times 10^{-3}T - c \times 10^5 T^{-2}$$

The right-hand side of the equation is evaluated for all experimental results and the values of $[(\Delta H_0/T) + I]$ are plotted *vs.* $1/T$. The slope of the best straight line through the points gives ΔH_0 and leads to a value of I. The values are given in the text together with those for the enthalpy, $\Delta H°$, free energy, $\Delta F°$, and entropy, $\Delta S°$, of reaction calculated for the temperature 298.15°K.

$VO_{2.17}$.—The reaction between vanadium pentoxide and sulfur dioxide was studied by Flood and Kleppa,[116] who supposed that the reduced form of the oxide, with unknown structure, had the composition VO_2. The composition $V_{12}O_{26}$, or $VO_{2.17}$, has been ascribed to this structure by Aebi,[117] and the entropy of reaction reported, $\Delta S_{298} = -1.6$ cal. °K.$^{-1}$, therefore was taken to apply to the reaction

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$$3VO_{2.5}(s) + SO_2(g) = 3VO_{2.17}(s) + SO_3(g)$$

With the available entropy data for $SO_2(g)$,[87] $SO_3(g)$,[87] and $VO_{2.5}$[43] the entropy of $VO_{2.17}$ at 298.15°K. is 14.4 cal. g.f.w.$^{-1}$ °K.$^{-1}$.

Mo_2S_3.—Stubbles and Richardson[118] studied the reaction

$$2/3\ Mo(s) + H_2S(g) = {}^1/_3\ Mo_2S_3(s) + H_2(g)$$

in the range 1119 to 1467°K. The data are evaluated here taking literature data[119] for the heat capacities of Mo(s), $H_2S(g)$, and $H_2(g)$, and assuming $C_p = 26.36 + 7.88 \times 10^{-3}T - 2.30 \times 10^5T^{-2}$ for $Mo_2S_3(s)$, *i.e.*, the same as earlier assumed[71] for Ir_2Se_3. This gives $\Delta C_p = 4.05 - 0.66 \times 10^{-3}T - 0.19 \times 10^5T^{-2}$ and $\Delta H_0 = -26{,}500$; $I = 39.04$; $\Delta H°_{298} = -25.25$ kcal.; $\Delta F°_{298} = -21.68$ kcal.; and $\Delta S°_{298} = -12.00$ cal. °K.$^{-1}$. The standard entropy of 1/2 $Mo_2S_3(s)$ at 298.15°K. is thus 15.7 cal. g.f.w.$^{-1}$ °K.$^{-1}$ on the basis of available entropy data[87] for Mo(s), $H_2(g)$, and $H_2S(g)$.

ReS_2.—Juza and Biltz[120] studied the reaction

$$ReS_2(s) = Re(s) + S_2(g)$$

measuring the sulfur pressures at T = 1383, 1462, and 1498°K. With heat capacity values of Re(s)[119] and $S_2(g)$[119] and assuming the same values for $ReS_2(s)$ as for $PtS_2(s)$,[71] $C_p = 16.39 + 3.77 \times 10^{-3}T - 1.57 \times 10^5T^{-2}$, the heat capacity change for the reaction is $\Delta C_p = -2.01 - 2.31 \times 10^{-3}T + 0.67 \times 10^5T^{-2}$. This gives $\Delta H_0 = 77{,}000$, $I = -63.75$, $\Delta H°_{298} = 76.07$ kcal., $\Delta F°_{298} = 61.40$ kcal., and $S°_{298} = 49.22$ cal. °K.$^{-1}$. On the basis of available entropy data for the elements[87] the standard entropy of $ReS_2(s)$ at 298.15°K. is 14.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$.

$CoS_{0.89}$.—The reaction

$$9Co(s) + 8H_2S(g) = Co_9S_8(s) + 8H_2(g)$$

was studied by Rosenqvist[121] in the range 873 to 1056°K. and the entropy of formation of $Co_9S_8(s)$ reported to be $\Delta S_f° = -64.8$ cal. °K.$^{-1}$ at 1000°K. Using the available entropy data[87,119] for Co(s), $H_2S(g)$, and $H_2(g)$, and assuming the entropy increment for $Co_9S_8(s)$ to be 130 cal. g.f.w.$^{-1}$ °K.$^{-1}$ between 298.15 and 1000°K., the standard entropy of 1/9 $Co_9S_8(s)$ at 298.15°K. is estimated to be 12.4 cal. g.f.w.$^{-1}$ °K.$^{-1}$. Kolbina, *et al.*,[122] report the entropy of formation of $CoS_{0.885}$ (s) to be $\Delta S_f° = -5.57$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 1068°K., presumably for the reaction $Co(s) + 0.885\ H_2S(g) = CoS_{0.885}(s) + 0.885\ H_2(g)$. Evaluation by a similar method on the assumption that the entropy increment for $CoS_{0.885}(s)$ is 15.5 cal. g.f.w.$^{-1}$ °K.$^{-1}$ between 298 and 1068°K., results in $S°_{298} = 13.8$ cal. g.f.w.$^{-1}$ °K.$^{-1}$. The mean value $S°_{298} = 13.1$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ for the standard entropy of 1/9 $Co_9S_8(s)$ is selected.

CoS.—Rosenqvist[121] arrived at an entropy value of 31.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 1000°K. The sulfide was not found to be thermodynamically stable below 460°, but is easily obtained in a metastable state. The standard entropy at 298.15°K. is estimated to be 15.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$ assuming the entropy increment between 298 and 1000°K. to be 16 cal. g.f.w.$^{-1}$ °K.$^{-1}$ for CoS(s). The entropy of reaction values (−2.31 and −2.46 cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 1068 and 1093°K., respectively) reported by Kolbina, *et al.*,[122] for

$$Co(s) + H_2S(g) = CoS(s) + H_2(g)$$

lead to the value $S°_{298} = 18.1$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ assuming the entropy increment between 298 and 1083°K. to be 17 cal. g.f.w.$^{-1}$ °K.$^{-1}$. This value is so high that it is disregarded.

$CoS_{1.33}$.—For this compound Rosenqvist[121] gave the entropy value $S°_{1000} = 33.6$ cal. g.f.w.$^{-1}$ °K.$^{-1}$. The complete lack of high temperature heat capacity data for sulfides of this composition makes interpolation difficult. Taking the entropy increment between 298 and 1000°K. to be 18 cal. g.f.w.$^{-1}$ °K.$^{-1}$, the estimated standard entropy of $CoS_{1.33}(s)$ is 15.6 cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 298.15°K.

CoS_2.—Hülsmann, Biltz, and Meisel[123] studied the decomposition of CoS_2, which is supposed to take place according to the reaction

$$2.25CoS_2(s) = 2.25CoS_{1.12}(s) + S_2(g)$$

Their data at 973, 1003, and 1033°K. are evaluated taking the $S_2(g)$ pressures to be 32, 86, 194 mm., respectively. The heat capacity change for the reaction is estimated as $\Delta C_p = -2.22 - 4.81 \times 10^{-3}T + 3.10 \times 10^5T^{-2}$, which leads to $\Delta H_0 = 64{,}000$, $I = -76.97$, $\Delta H°_{298} = 62.09$ kcal., $\Delta F°_{298} = 44.51$ kcal., and $\Delta S°_{298} = 58.95$ cal. °K.$^{-1}$. From the standard entropy values for $S_2(g)$[87] and for $CoS_{1.12}(s)$ equal to that of CoS(s), the value for $CoS_2(s)$ is $S°_{298} = 13.8$ cal. g.f.w.$^{-1}$ °K.$^{-1}$. Rosenqvist[121] reported data for the reaction

$${}^1/_2Co_3S_4(s) + H_2S(g) = {}^3/_2CoS_2(s) + H_2(g)$$

in the temperature range 642 to 873°K. The heat capacity change for the reaction is assumed to be $\Delta C_p = 5.97 + 1.15 \times 10^{-3}T - 2.09 \times 10^5T^{-2}$, which leads to $\Delta H_0 = 12{,}500$, $I = 61.35$, $\Delta H°_{298} = -9.97$ kcal., $\Delta F°_{298} = -4.05$ kcal., and $\Delta S°_{298} = -19.84$ cal. °K.$^{-1}$. This results in an entropy difference of $S°_{CoS_2(s)} - S°_{CoS_{1.33}(s)} = -1.3$ at 298.15°K. and of $S°_{298} = 14.3$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ for CoS_2 (s). The mean value 13.7 cal. g.f.w.$^{-1}$ °K.$^{-1}$ is chosen.

$RhO_{1.5}$.—Wöhler and Müller[124] studied the thermal decomposition of Rh_2O_3, which they assumed resulted in the formation of lower rhodium oxides with composition RhO and Rh_2O. The existence of the oxide Rh_2O was refuted by Schenck and Finkener,[125] and independent evidence about the oxide RhO still is lacking. Thus, the decomposition of Rh_2O_3 is assumed to take place according to the equation

$${}^4/_3RhO_{1.5}(s) = {}^4/_3Rh(s) + O_2(g)$$

Evaluation of the data by Wöhler and Müller for oxides with gross compositions RhO and RhO_2 with the heat capacity change taken[119] as $\Delta C_p = 0.64 - 5.45 \times 10^{-3}T - 0.40 \times 10^5T^{-2}$ gives $\Delta H_0 = 62{,}500$, $I = -44.02$,

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$\Delta H°_{298} = 62.58$ kcal., $\Delta F°_{298} = 48.60$ kcal., and $\Delta S°_{298} = 46.90$ cal. °K.$^{-1}$. Incorporating the available entropy data[87] for Rh(s) and O_2(g), the standard entropy of $RhO_{1.5}$ becomes 9.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 298.15°K.

IrO_2.—St.-Claire Deville and Debray,[126] Wöhler and Witzmann,[127] and Schäfer and Heitland[128] have studied the reaction

$$IrO_2(s) = Ir(s) + O_2(g)$$

in the range 1076 to 1412°K. The heat capacity change for the reaction is taken[119] as $\Delta C_p = 3.65 - 12.78 \times 10^{-3}T - 0.40 \times 10^5T^{-2}$, leading to $\Delta H_0 = 55{,}200$, $I = -22.09$, $\Delta H°_{298} = 55.85$ kcal., $\Delta F°_{298} = 43.05$ kcal., and $\Delta S°_{298} = 42.95$ cal. °K.$^{-1}$. The standard entropy of IrO_2(s) at 298.15°K. is thus 14.6 cal. g.f.w.$^{-1}$ °K.$^{-1}$ on the basis of available entropy data[87] for Ir(s) and O_2(g).

$NiS_{0.67}$.—Data[121] for the reaction

$$^3/_2Ni(s) + H_2S(g) = {}^1/_2Ni_3S_2(s) + H_2(g)$$

at temperatures from 667 to 808°K. are evaluated by taking the heat capacity change for the reaction to be $\Delta C_p = 3.59 + 4.72 \times 10^{-3}T + 0.58 \times 10^5T^{-2}$ above 633°K. The values of the integration constants are: $\Delta H_0 = -20{,}800$, $I = 37.53$. For $\Delta S°_{298}$ the calculated value (−12.40 cal. °K.$^{-1}$) refers to a hypothetical state for Ni(s) because the entropy of the magnetic transition has been neglected in the extrapolation to 298°K. This 0.29 cal. g. atom^{-1} °K.$^{-1}$ is added to the standard entropy of nickel at 298°K. to give $S°_{298} = 11.1$ cal. °K.$^{-1}$ for one gram formula weight of $NiS_{0.67}$.

NiS.—For this compound Rosenqvist[121] gives $S°_{1000} = 31.3$ cal. g.f.w.$^{-1}$ °K.$^{-1}$, and also $\Delta H_f°$ and $\Delta F_f°$ values at 298°K. for the reaction Ni + S(rh) = NiS. Assuming the entropy increment between 298 and 1000°K. to be 15.5 cal. g.f.w.$^{-1}$ °K.$^{-1}$, with one additional entropy unit for the transition NiS(rh) → NiS(h) at 669°K., the standard entropies at 298.15°K. are 14.8 and 15.8 cal. g.f.w.$^{-1}$ °K.$^{-1}$ for NiS(rh) and NiS(h), respectively. The enthalpy and free energy of formation values for NiS by Rosenqvist[121] lead to $S°_{298} = 16.1$ cal. g.f.w.$^{-1}$ °K.$^{-1}$.

NiS_2.—The reaction

$$2.14NiS_2(s) = 2.14NiS_{1.07}(h) + S_2(g)$$

was studied by Biltz, Voigt, and Meisel[129] in the range 923 to 1033°K. For evaluating the data the heat capacity change is estimated to be $\Delta C_p = -6.55 + 13.07 \times 10^{-3}T + 2.46 \times 10^5T^{-2}$. With p_{S_2} equal to 32, 124, 192, 253, and 475 mm. at 923, 973, 993, 1003, and 1033°K., respectively, the best values for the integration constants are $\Delta H_0 = 46{,}800$ and $I = -82.97$. At 298.15°K. the entropy difference $S°_{NiS_2(s)} - S°_{NiS_{1.07}(h)} = 6.0$ cal. g.f.w.$^{-1}$ °K.$^{-1}$. This leads to such a high entropy value for NiS_2 (22 cal. g.f.w.$^{-1}$ °K.$^{-1}$) that it is disregarded.

The related reaction

$$1.07NiS_2(s) + H_2(g) = 1.07NiS_{1.07}(h) + H_2S(g)$$

was studied by Rosenqvist[121] in the range 673 to 873°K. With the heat capacity increment $\Delta C_p = -6.35 + 5.00 \times 10^{-3}T + 1.09 \times 10^5T^{-2}$, the values of the integration constants are found to be $\Delta H_0 = 7{,}200$ and $I = -56.6$. This leads to the entropy difference $S°_{NiS_2(s)} - S°_{NiS_{1.07}(h)} = 2.7$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ at 298.15°K. Using the value for $S_{298} = 16$ cal. g.f.w.$^{-1}$ °K.$^{-1}$ for $NiS_{1.07}$(h), the resulting mean value for the entropy of NiS_2(s) is $S°_{298} = 18.7$ cal. g.f.w.$^{-1}$ °K.$^{-1}$. This value agrees well with that obtained from Rosenqvist's entropy value at 1000°K. (38.2 cal. g.f.w.$^{-1}$ °K.$^{-1}$), assuming the entropy increment between 298 and 1000°K. to be 20 cal. g.f.w.$^{-1}$ °K.$^{-1}$. The average value for the standard entropy of NiS_2(s), 18.5 cal. g.f.w.$^{-1}$ °K.$^{-1}$, at 298.15°K. is chosen.

PdO.—Wöhler[130] and Schenck and Kurzen[131] studied the reaction

$$2PdO(s) = 2Pd(s) + O_2(g)$$

at temperatures from 958 to 1150°K. The heat capacity change for the reaction is taken[119] to be $\Delta C_p = 12.16 - 24.64 \times 10^{-3}T - 0.40 \times 10^5T^{-2}$ leading for the combined data to $\Delta H_0 = 51{,}400$, $I = 26.63$, $\Delta H°_{298} = 54.07$ kcal., $\Delta F°_{298} = 39.84$ kcal., and $\Delta S°_{298} = 47.69$ cal. °K.$^{-1}$. The standard entropy of PdO(s) at 298.15°K. is thus 9.7 cal. g.f.w.$^{-1}$ °K.$^{-1}$ on the basis of available entropy data[87] for Pd(s) and O_2(g).

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