$S°(298.15\ K) = 29.870 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_t = 631 \pm 1\ K$
$T_{fus} = 1728 \pm 4\ K$

$\Delta_f H°(0\ K) = 0\ k\ J·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H° = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.15 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity values are based primarily on the studies by Keesom and Clark[1] and Busey and Giauque.[2] The adopted values are actually those suggested by Busey and Giauque[2] with slight changes above 280 K so as to smoothly join the high temperature heat capacity data.

There are numerous heat capacity studies in the vicinity of the Curie point. The studies upon which our adopted values are based are as follows:

Source	Year	T, K
[3]	1938	343–1123
[4]	1955	453–1437
[5]	1965	323–883
[6]	1966	300–1728
[7]	1966	571–681
[8]	1970	333–1500
[9]	1971	580–680

The adoped value for the Curie point, $T_c = 631$ K, is from the study of Connelly *et al.*,[9] using an AC calorimetric method to measure relative heat capacity values, and Vollmer *et al.*[6] using a high temperature adiabatic calorimeter.

Above 700 K, the adopted heat capacity values are those reported by Vollmer *et al.*[6] Below the Curie point, the above studies and that of Bronson and Wilson (203–383 K)[10] are used to construct a curve which joins smoothly with the low temperature values. The adopted table is identical (purposely) to that suggested by Mah and Pankatz.[11]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K)$, is calculated as the difference between $\Delta_f H°(298.15\ K)$ for Ni(g) and Ni(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−4.786	0.	0.	0.
100	13.631	7.454	50.235	−4.278	0.	0.	0.
200	22.468	20.200	32.143	−2.389	0.	0.	0.
250	24.397	25.432	30.290	−1.215	0.	0.	0.
298.15	25.987	29.870	29.870	0.	0.	0.	0.
300	26.024	30.031	29.871	0.048	0.	0.	0.
350	27.294	34.139	30.192	1.381	0.	0.	0.
400	28.493	37.863	30.922	2.776	0.	0.	0.
450	29.623	41.281	31.886	4.228	0.	0.	0.
500	31.045	44.473	32.986	5.743	0.	0.	0.
600	34.853	50.440	35.404	9.022	0.	0.	0.
631.000	39.832	52.263	36.187	10.144	C_p, LAMBDA MAXIMUM		
631.000	39.832	52.263	36.187	10.144	TRANSITION		
700	30.794	55.575	37.941	12.344	0.	0.	0.
800	31.003	59.697	40.408	15.431	0.	0.	0.
900	31.589	63.382	42.759	18.560	0.	0.	0.
1000	32.217	66.742	44.992	21.750	0.	0.	0.
1100	32.928	69.845	47.112	25.007	0.	0.	0.
1200	33.681	72.742	49.128	28.336	0.	0.	0.
1300	34.518	75.471	51.051	31.746	0.	0.	0.
1400	35.397	78.061	52.888	35.241	0.	0.	0.
1500	36.317	80.534	54.649	38.827	0.	0.	0.
1600	37.279	82.908	56.342	42.506	0.	0.	0.
1700	38.284	85.199	57.972	46.286	0.	0.	0.
1728.000	38.535	85.827	58.419	47.361	--- CRYSTAL <--> LIQUID ---		
1800	39.330	87.411	59.547	50.156	−17.161	0.715	−0.021
1900	42.677	89.637	61.072	54.275	−16.933	1.704	−0.047
2000	43.806	91.855	62.556	58.599	−16.501	2.674	−0.070
2100	44.978	94.021	64.003	63.038	−15.953	3.620	−0.090
2200	46.191	96.141	65.415	67.596	−15.286	4.536	−0.108
2300	47.447	98.222	66.797	72.278	−14.495	5.420	−0.123
2400	48.702	100.268	68.149	77.085	−13.579	6.267	−0.136
2500	49.957	102.281	69.474	82.018	−12.537	7.073	−0.148

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = [41.487] J·K^{-1}·mol^{-1}$
$T_{fus} = 1728 \pm 4\ K$

$\Delta_f H°(298.15\ K) = [17.479]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.15 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Ni(l) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1728) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Vollmer *et al.*,[1] using an adiabatic high temperature calorimeter with an inert gas atmosphere, measured the heat capcity of nickel in the liquid region (1728–1822 K) and reported $C_p°(l) = 9.32\ kcal·mol^{-1}$. Other studies yielding liquid phase heat capacity values are: 7.86 $kcal·mol^{-1}$ by Wüst *et al.*,[2] 9.2 $kcal·mol^{-1}$ by Umino,[3] 10.3 $kcal·mol^{-1}$ by Geoffray *et al.*,[4] and 2.58 $kcal·mol^{-1}$ by Margrave.[5] This latter value[5] is undoubtedly a misprint.

We adopt a constant value, $C_p°(l) = 9.3\ kcal·mol^{-1}$ based on the heat capacity measurements of Vollmer *et al.*[1] The enthalpy study of Geoffray *et al.*[4] (1393–2192 K) leads to a reported heat capacity whilch is roughly 10% higher than our adopted value. The adopted value is identical to that chosen by Mah and Pankratz.[6]

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted melting point, $T_{fus} = 1728 \pm 4$ K (based on IPTS–68), is selected from the studies of Vollmer *et al.* (1727 K),[1] Geoffray *et al.*[4] (1728 K), Oriani and Jones (1727 K),[7] and Kubachewski (1730 K).[8]

The adopted enthalpy of melting, $\Delta_{fus}H° = 4.10 \pm 0.1\ kcal·mol^{-1}$, is based on the calorimetric studies by Vollmer *et al.* ($4.039 \pm 0.060\ kcal·mol^{-1}$) and Geoffray *et al.* ($4.176 \pm 054\ kcal·mol^{-1}$). Other reported results are 3.31 $kcal·mol^{-1}$ by Wüst *et al.*,[2] 4.21 $kcal·mol^{-1}$ by Umino,[3] 3.32 $kcal·mol^{-1}$ by Margrave,[5] and 4.4 $kcal·mol^{-1}$ by Lebedev *et al.*[9]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	26.133	41.487	41.487	0.	17.479	14.016	−2.456
300	26.150	41.648	41.487	0.048	17.480	13.994	−2.437
350	26.568	45.711	41.807	1.366	17.464	13.414	−2.002
400	26.987	49.286	42.523	2.705	17.408	12.839	−1.677
450	27.405	52.489	43.455	4.065	17.316	12.273	−1.425
500	27.824	55.398	44.506	5.446	17.182	11.719	−1.224
600	28.660	60.544	46.761	8.270	16.728	10.665	−0.928
700	29.497	65.025	49.057	11.178	16.313	9.698	−0.724
800	30.334	69.019	51.307	14.169	16.218	8.760	−0.572
900	31.171	72.640	53.479	17.245	16.164	7.831	−0.455
1000	32.008	75.967	55.564	20.404	16.133	6.907	−0.361
1100	32.844	79.057	57.561	23.646	16.119	5.986	−0.284
1200	33.681	81.951	59.474	26.972	16.115	5.065	−0.220
1300	34.518	84.680	61.309	30.382	16.116	4.144	−0.166
1300.000	34.518	84.680	61.309	30.382	GLASS <--> LIQUID		
1300.000	38.911	84.680	61.309	30.382	TRANSITION		
1400	38.911	87.564	63.083	34.273	16.511	3.207	−0.120
1500	38.911	90.248	64.805	38.165	16.817	2.246	−0.078
1600	38.911	92.759	66.475	42.056	17.029	1.267	−0.041
1700	38.911	95.118	68.091	45.947	17.140	0.278	−0.009
1728.000	38.911	95.754	68.534	47.036	--- CRYSTAL <--> LIQUID ---		
1800	38.911	97.343	69.655	49.838	0.	0.	0.
1900	38.911	99.446	71.168	53.729	0.	0.	0.
2000	38.911	101.442	72.632	57.620	0.	0.	0.
2100	38.911	103.341	74.050	61.511	0.	0.	0.
2200	38.911	105.151	75.423	65.402	0.	0.	0.
2300	38.911	106.881	76.753	69.294	0.	0.	0.
2400	38.911	108.537	78.043	73.185	0.	0.	0.
2500	38.911	110.125	79.295	77.076	0.	0.	0.
2600	38.911	111.651	80.510	80.967	0.	0.	0.
2700	38.911	113.120	81.691	84.858	0.	0.	0.
2800	38.911	114.535	82.839	88.749	0.	0.	0.
2900	38.911	115.900	83.955	92.640	0.	0.	0.
3000	38.911	117.219	85.042	96.531	0.	0.	0.
3100	38.911	118.495	86.101	100.423	0.	0.	0.
3156.584	38.911	119.199	86.688	102.624	----- FUGACITY = 1 bar -----		
3200	38.911	119.731	87.133	104.314	−376.835	5.189	−0.085
3300	38.911	120.928	88.139	108.205	−375.182	17.101	−0.271
3400	38.911	122.090	89.120	112.096	−373.527	28.964	−0.445
3500	38.911	123.218	90.078	115.987	−371.873	40.778	−0.609
3600	38.911	124.314	91.014	119.878	−370.219	52.544	−0.762

PREVIOUS: CURRENT: December 1976

CRYSTAL-LIQUID

0 to 1728 K crystal
above 1728 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−4.786	0.	0.	0.
100	13.631	7.454	50.235	−4.278	0.	0.	0.
200	22.468	20.200	32.143	−2.389	0.	0.	0.
250	24.397	25.432	30.290	−1.215	0.	0.	0.
298.15	25.987	29.870	29.870	0.	0.	0.	0.
300	26.024	30.031	29.871	0.048	0.	0.	0.
350	27.294	34.139	30.192	1.381	0.	0.	0.
400	28.493	37.863	30.922	2.776	0.	0.	0.
450	29.623	41.281	31.886	4.228	0.	0.	0.
500	31.045	44.473	32.986	5.743	0.	0.	0.
600	34.853	50.440	35.404	9.022	0.	0.	0.
631.000	39.832	52.263	36.187	10.144	——— C_p LAMBDA MAXIMUM ———		
631.000	39.832	52.263	36.187	10.144	TRANSITION		
700	30.794	55.575	37.941	12.344	0.	0.	0.
800	31.003	59.697	40.408	15.431	0.	0.	0.
900	31.589	63.382	42.759	18.560	0.	0.	0.
1000	32.217	66.742	44.992	21.750	0.	0.	0.
1100	32.928	69.845	47.112	25.007	0.	0.	0.
1200	33.681	72.742	49.128	28.336	0.	0.	0.
1300	34.518	75.471	51.051	31.746	0.	0.	0.
1400	35.397	78.061	52.888	35.241	0.	0.	0.
1500	36.317	80.534	54.649	38.827	0.	0.	0.
1600	37.279	82.908	56.342	42.506	0.	0.	0.
1700	38.284	85.199	57.972	46.286	0.	0.	0.
1728.000	38.535	85.827	58.419	47.361	——— CRYSTAL <--> LIQUID ———		
1728.000	38.911	95.754	58.419	64.516	TRANSITION		
1800	38.911	97.343	59.944	67.317	0.	0.	0.
1900	38.911	99.446	61.968	71.208	0.	0.	0.
2000	38.911	101.442	63.893	75.099	0.	0.	0.
2100	38.911	103.341	65.726	78.991	0.	0.	0.
2200	38.911	105.151	67.477	82.882	0.	0.	0.
2300	38.911	106.881	69.153	86.773	0.	0.	0.
2400	38.911	108.537	70.760	90.664	0.	0.	0.
2500	38.911	110.125	72.303	94.555	0.	0.	0.
2600	38.911	111.651	73.787	98.446	0.	0.	0.
2700	38.911	113.120	75.217	102.337	0.	0.	0.
2800	38.911	114.535	76.596	106.228	0.	0.	0.
2900	38.911	115.900	77.928	110.120	0.	0.	0.
3000	38.911	117.219	79.216	114.011	0.	0.	0.
3100	38.911	118.495	80.462	117.902	0.	0.	0.
3156.584	38.911	119.199	81.151	120.104	----- FUGACITY = 1 bar -----		
3200	38.911	119.731	81.670	121.793	−376.835	5.189	−0.085
3300	38.911	120.928	82.842	125.684	−375.182	17.101	−0.271
3400	38.911	122.090	83.979	129.575	−373.527	28.964	−0.445
3500	38.911	123.218	85.084	133.466	−371.873	40.778	−0.609
3600	38.911	124.314	86.159	137.357	−370.219	52.544	−0.762

PREVIOUS: CURRENT: December 1976

IP(Ni, g) = 61579 ± 10 cm^{-1}
$S°(298.15\ K) = 182.190 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 428.1 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 430.1 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0.00	9
$^3D_3$	204.786	7
$^3D_2$	879.813	5
$^3F_3$	1332.153	7
$^3D_1$	1713.080	3
$^3F_2$	2216.519	5

Enthalpy of Formation

The enthalpy of formation for Ni(g) is obtained by an analysis of the vapor pressure data of Morris *et al.*[1] In this study a gas–transport method was used to measure vapor pressures (16 points) over liquid nickel in the range 1816–1895 K. For this vaporization process, we obtain $\Delta_{vap}H°(298.15\ K) = 99.33 \pm 1.23\ kcal \cdot mol^{-1}$ (2nd law) and $98.54 \pm 0.12\ cal \cdot mol^{-1}$ (3rd law). The entropy difference (2nd law–3rd law) is only $-0.04 \pm 0.7\ cal \cdot K^{-1} \cdot mol^{-1}$ which suggests good consistency between our adopted functions and the vapor pressure data. Using the 3rd law $\Delta_{vap}H°(298.15\ K)$ and $\Delta_f H°(Ni, l, 298.15\ K)$,[2] we calculate and adopt $\Delta_f H°(Ni, g, 298.15\ K) = 102.8\ kcal \cdot mol^{-1}$. [This is the same value chosen by Hultgren *et al.*[4] and Mah and Pankratz.[5] Thus we maintain closer similarity with the most recent tabulations.]

Using mass spectrometric intensity data, Farber and Srivastava[3] obtained a 2nd law enthalpy of sublimation of 99.4 $kcal \cdot mol^{-1}$ at an average temperature of 1653 K and a 2nd law enthalpy of vaporization of 92.2 $kcal \cdot mol^{-1}$ at an average temperature of 1863 K. Using auxiliary data,[2] we calculate $\Delta_f H°(Ni, l, 298.15\ K) = 102.1\ kcal \cdot mol^{-1}$ and 99.8 $kcal \cdot mol^{-1}$ respectively. Rutner and Haury[6] measured vapor pressures over Ni (28 points in the range 1277–1658 K), using the Langmuir technique. Their results yield a 2nd law value of $107.0 \pm 5.8\ kcal \cdot mol^{-1}$ and a 3rd law value of $103.2 \pm 4.0\ kcal \cdot mol^{-1}$. The drift is $-2.5 \pm 3.9\ cal \cdot K^{-1} \cdot mol^{-1}$. In addition Rutner and Haury[6] determined the best values of the heat of sublimation and vaporization and the parameters in a vapor pressure equation by statistically weighting nine sets of data. Although the results of this statistical treatment lead to enthalpies of formation for Ni(g) consistent with the adopted value, the results are not consistent with the melting data. Other vapor pressure studies are discussed by Hultgren *et al.*[4]

Heat Capacity and Entropy

The electronic energy levels and quantum weights used in the calculation are from Moore[7] and Roth.[8] Not all levels are listed above. The tabulated entropy values agree within 0.001 $cal \cdot K^{-1} \cdot mol^{-1}$ with the recent tabulation by Hultgren *et al.*[4] and Mah and Pankratz.[5] There are predicted levels which have not been observed and/or classified. It is not expected that $S°(298.15\ K)$ would be affected by these states, but that in the range 3000–6000 K, an error of 0.2–0.3 $cal \cdot K^{-1} \cdot mol^{-1}$ might result. In our present tabulation, the levels above 20000 cm^{-1} contribute 0.0005 $cal \cdot K^{-1} \cdot mol^{-1}$ at 3000 K and 0.15 $cal \cdot K^{-1} \cdot mol^{-1}$ at 6000 K to the entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−6.825	428.076	428.076	INFINITE
100	23.510	156.498	203.000	−4.650	429.743	414.839	−216.690
200	23.396	172.882	184.321	−2.288	430.216	399.680	−104.386
250	23.275	178.085	182.574	−1.122	430.208	392.044	−81.913
298.15	23.360	182.190	182.190	0.	430.115	384.701	−67.398
300	23.367	182.334	182.190	0.043	430.110	384.419	−66.933
350	23.587	185.952	182.475	1.217	429.951	376.816	−56.237
400	23.859	189.119	183.112	2.403	429.742	369.239	−48.218
450	24.131	191.945	183.939	3.603	429.490	361.691	−41.984
500	24.374	194.500	184.870	4.815	429.187	354.174	−37.000
600	24.734	198.979	186.858	7.272	428.366	339.243	−29.534
700	24.925	202.808	188.870	9.756	427.528	324.465	−24.212
800	24.981	206.141	190.825	12.253	426.937	309.782	−20.227
900	24.942	209.082	192.693	14.749	426.305	295.174	−17.131
1000	24.841	211.705	194.466	17.239	425.605	280.641	−14.659
1100	24.701	214.066	196.142	19.716	424.825	266.182	−12.640
1200	24.538	216.209	197.726	22.178	423.957	251.797	−10.960
1300	24.364	218.166	199.225	24.624	422.993	237.489	−9.542
1400	24.187	219.965	200.643	27.051	421.925	223.259	−8.330
1500	24.012	221.628	201.987	29.461	420.750	209.109	−7.282
1600	23.842	223.172	203.263	31.854	419.463	195.041	−6.367
1700	23.679	224.612	204.477	34.230	418.059	181.057	−5.563
1800	23.524	225.961	205.634	36.590	399.388	167.874	−4.872
1900	23.380	227.229	206.737	38.935	397.842	155.054	−4.263
2000	23.245	228.425	207.792	41.266	396.282	142.316	−3.717
2100	23.121	229.556	208.802	43.584	394.709	129.656	−3.225
2200	23.007	230.629	209.770	45.891	393.124	117.072	−2.780
2300	22.903	231.650	210.699	48.186	391.528	104.560	−2.375
2400	22.810	232.622	211.592	50.472	389.923	92.117	−2.005
2500	22.725	233.552	212.452	52.748	388.308	79.742	−1.666
2600	22.651	234.441	213.281	55.017	386.686	67.431	−1.355
2700	22.585	235.295	214.081	57.279	385.057	55.183	−1.068
2800	22.529	236.115	214.853	59.534	383.421	42.996	−0.802
2900	22.481	236.905	215.600	61.785	381.780	30.866	−0.556
3000	22.441	237.667	216.323	64.031	380.135	18.794	−0.327
3100	22.410	238.402	217.023	66.273	378.487	6.776	−0.114
3156.584	22.396	238.807	217.410	67.541	----- FUGACITY = 1 bar -----		
3200	22.388	239.113	217.703	68.513	0.	0.	0.
3300	22.373	239.802	218.362	70.751	0.	0.	0.
3400	22.366	240.469	219.002	72.988	0.	0.	0.
3500	22.368	241.118	219.625	75.225	0.	0.	0.
3600	22.377	241.748	220.231	77.462	0.	0.	0.
3700	22.395	242.361	220.821	79.700	0.	0.	0.
3800	22.421	242.959	221.395	81.941	0.	0.	0.
3900	22.456	243.542	221.956	84.185	0.	0.	0.
4000	22.499	244.111	222.503	86.433	0.	0.	0.
4100	22.551	244.667	223.036	88.685	0.	0.	0.
4200	22.611	245.211	223.558	90.943	0.	0.	0.
4300	22.681	245.744	224.068	93.208	0.	0.	0.
4400	22.761	246.266	224.566	95.480	0.	0.	0.
4500	22.850	246.779	225.054	97.760	0.	0.	0.
4600	22.949	247.282	225.532	100.050	0.	0.	0.
4700	23.058	247.777	226.000	102.350	0.	0.	0.
4800	23.178	248.263	226.459	104.662	0.	0.	0.
4900	23.309	248.743	226.909	106.986	0.	0.	0.
5000	23.451	249.215	227.350	109.324	0.	0.	0.
5100	23.604	249.681	227.783	111.677	0.	0.	0.
5200	23.769	250.141	228.209	114.045	0.	0.	0.
5300	23.947	250.595	228.627	116.431	0.	0.	0.
5400	24.136	251.045	229.038	118.835	0.	0.	0.
5500	24.339	251.489	229.442	121.258	0.	0.	0.
5600	24.555	251.930	229.840	123.703	0.	0.	0.
5700	24.784	252.366	230.231	126.170	0.	0.	0.
5800	25.028	252.799	230.617	128.660	0.	0.	0.
5900	25.287	253.229	230.996	131.176	0.	0.	0.
6000	25.560	253.657	231.370	133.718	0.	0.	0.

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

IP(Ni^+, g) = 146541.56 ± 0.02 cm^{-1}
$S°(298.15\ K)$ = 199.72 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 1164.98 ± 8.4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [1179.003] $kJ·mol^{-1}$

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2D_{5/2}$	0.00	6
$^2D_{3/2}$	1606.94	4

Enthalpy of Formation

$\Delta_f H°(Ni^+, g, 0\ K)$ is calculated from $\Delta_f H°(Ni, g, 0\ K)$[1] using the spectroscopic value of IP(Ni) = 61600 ± 10 cm^{-1} (736.90 ± 0.12 $kJ·mol^{-1}$) from Corliss and Sugar.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ni^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Ni, g, 0\ K)$ by using IP(Ni) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Ni(g), $Ni^+(g)$, and e^-(ref). $\Delta_f H°(Ni \rightarrow Ni^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground state for $Ni^+(g)$, all levels listed by Corliss and Sugar[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for $Ni^+(g)$, the thermodynamic functions are dependent of the estimated missing levels (for n > 3) and the cut–off procedure, the Gibbs energy function shows variations of ~20% at 1000 K. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, and the fundamental constants Extension of these calculations aboue 6000 K may require consideration of the higher excited states (n > 5), and use of different fill and cut–off procedures.[6]

References

[1]JANAF Thermochemical Tables· Ni(g), 12–31–76; e^-(ref), 3–31–82.
[2]C. Corliss and J. Sugar, J. Phys. Chem. Ref. Data **10**, 197 (1981).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[5]R. D. Levin and S. G. Lias, U.S. Nat. Bur. Stand., NSRDS–NBS–71, 634 pp. (1982).
[6]J R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–78–0960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.615	1164.976		
100	20.787	151.833	257.198	−10.537			
200	35.551	167.752	208.658	−8.181			
250	86.780	180.587	201.615	−5.257			
298.15	121.588	199.724	199.724	0.	1179.003	1122.106	−196.588
300	121.596	200.476	199.726	0.225	1179.218	1121.752	−195.314
350	96.043	217.764	201.149	5.815	1184.514	1111.737	−165.918
400	62.862	228.293	203.945	9.739	1188.082	1101.076	−143.786
450	43.263	234.441	207.020	12.339	1190.270	1090.058	−126.531
500	33.285	238.423	209.973	14.225	1191.680	1078.842	−112.706
600	25.407	243.650	215.183	17.080	1193.335	1056.100	−91.942
700	22.887	247.345	219.525	19.474	1194.485	1033.143	−77.094
800	21.897	250.327	223.195	21.706	1195.709	1010.009	−65.947
900	21.442	252.877	226.354	23.870	1196.823	986.729	−57.268
1000	21.206	255.122	229.121	26 002	1197.843	963.329	−50.319
1100	21.072	257.137	231.578	28.115	1198.778	939.832	−44.629
1200	20.991	258.967	233.785	30.218	1199.630	916.253	−39.883
1300	20.939	260.645	235.788	32.314	1200.395	892.607	−35.865
1400	20.904	262.195	237.619	34.406	1201.070	868.905	−32.419
1500	20.879	263.636	239.306	36.495	1201.653	845.158	−29.431
1600	20.862	264.983	240.869	38.582	1202.139	821.375	−26.815
1700	20.849	266.248	242.325	40.668	1202.523	797.565	−24.506
1800	20.840	267.439	243.688	42.752	1185.655	774.450	−22.474
1900	20.833	268.566	244.968	44.836	1185.926	751.598	−20.663
2000	20.828	269.634	246.175	46.919	1186.197	728.732	−19.033
2100	20.824	270.650	247.316	49.002	1186 467	705.852	−17.557
2200	20.821	271.619	248.399	51.084	1186.737	682.959	−16.216
2300	20.819	272.544	249.429	53.166	1187.006	660.054	−14.990
2400	20.818	273.430	250.410	55.248	1187.275	637.137	−13.867
2500	20.817	274.280	251.348	57.329	1187.545	614.209	−12.833
2600	20.816	275.097	252.246	59.411	1187.814	591.271	−11.879
2700	20.816	275.882	253.107	61.493	1188.083	568.321	−10.995
2800	20.815	276.639	253.934	63.574	1188.352	545.362	−10.174
2900	20.815	277.370	254.730	65.656	1188.621	522.394	−9.409
3000	20.816	278.075	255.496	67.737	1188.890	499.416	−8.696
3100	20.816	278.758	256.236	69.819	1189.159	476.429	−8.028
3200	20.816	279.419	256.950	71.900	812.593	458.622	−7.486
3300	20.817	280.059	257.640	73.982	814.515	447.531	−7.084
3400	20.817	280.681	258.309	76.064	816.439	436.381	−6.704
3500	20.817	281.284	258.957	78.145	818.363	425.175	−6.345
3600	20.818	281.871	259.585	80.227	820.286	413.914	−6.006
3700	20.819	282.441	260.195	82.309	822.208	402.599	−5.684
3800	20.819	282.996	260.788	84.391	824.127	391.233	−5.378
3900	20.820	283.537	261.364	86.473	826.044	379.816	−5.087
4000	20.820	284.064	261.925	88.555	827.957	368.349	−4.810
4100	20.821	284.578	262.472	90.637	829.865	356.836	−4.546
4200	20.822	285.080	263.004	92.719	831.768	345.275	−4.294
4300	20.822	285.570	263.523	94.801	833.664	333.670	−4.053
4400	20.823	286.049	264.030	96.883	835.553	322.020	−3.823
4500	20.823	286.517	264.524	98.966	837.434	310.328	−3.602
4600	20.824	286.974	265.007	101.048	839.305	298.594	−3.391
4700	20.824	287.422	265.479	103.131	841.165	286.819	−3.188
4800	20.825	287.861	265.941	105.213	843.015	275.005	−2.993
4900	20.826	288.290	266.393	107.296	844.852	263.152	−2.805
5000	20.826	288.711	266.835	109.378	846.675	251.262	−2.625
5100	20.827	289.123	267.268	111.461	848.483	239.336	−2.451
5200	20.827	289.528	267.692	113.543	850.276	227.374	−2.284
5300	20.828	289.924	268.108	115.626	852.052	215.379	−2.123
5400	20.828	290.314	268.516	117.709	853.809	203.349	−1.967
5500	20.829	290.696	268.915	119.792	855.547	191.288	−1.817
5600	20.829	291.071	269.308	121.875	857.264	179.195	−1.671
5700	20.830	291 440	269.693	123.958	858.959	167.071	−1.531
5800	20.830	291.802	270.071	126.041	860.630	154.918	−1.395
5900	20 831	292.158	270.442	128.124	862.276	142.737	−1.264
6000	20.831	292.508	270.807	130.207	863.896	130.527	−1.136

PREVIOUS: CURRENT: June 1984 (1 bar)

EA(Ni, g) = 1.156 ± 0.010 eV
$S°(298.15\ K) = 174.577 \pm 0.005\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 316.5 \pm 1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [311.764]\ kJ·mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2D_{5/2}$	0	6
$^1D_{3/2}$	1470	4

Enthalpy of Formation

$\Delta_f H°(N,^-, g, 0\ K)$ is calculated from $\Delta_f H°(Ni, g, 0\ K)$[1] using the adopted electron affinity of EA (Ni) = 1.156 ± 0.010 eV (111.546 ± 0.965 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3]

Additional information on $Ni^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6] $\Delta_f H°(Ni^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ni, g, 0\ K)$ by using EA(Ni) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $Ni^-(g)$, Ni(g), and e^-(ref). $\Delta_r H°(Ni^- \rightarrow Ni + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $Ni^-(g)$ is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] and Masey.[6] The fine structure separation has been measured experimentally be laser photodetachment electron spectrometry[3] and is that recommended by Hotop and Lineberger.[2]

References

[1]JANAF Thermochemical Tables: Ni(g), 12–31–76; e ($^-$g), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, J. Phys. Chem. Ref. Data 14, 731 (1985).
[3]R. R. Corderman, P. C. Engleking and W. C. Lineberger, J. Chem. Phys. 70, 4474 (1979).
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[5]H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data 6, Supp. 1, 783 pp. (1977).
[6]H. S. W. Massey, "Negative Ions", 3rd., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.207	316.540		
100	20.786	151.833	193.117	−4.128			
200	20.802	166.242	176.490	−2.050			
250	20.870	170.890	174.922	−1.008			
298.15	21.017	174.577	174.577	0.	311.764	274.874	−48.157
300	21.025	174.707	174.578	0.039	311.716	274.646	−47.820
350	21.265	177.965	174.834	1.096	310.401	268.570	−40.082
400	21.564	180.824	175.408	2.166	309.037	262.687	−34.303
450	21.886	183.382	176.154	3.253	307.632	256.977	−29.829
500	22.202	185.705	176.995	4.355	306.180	251.427	−26.266
600	22.737	189.802	178.797	6.603	303.071	240.763	−20.960
700	23.099	193.337	180.627	8.896	299.963	230.634	−17.210
800	23.297	196.436	182.414	11.217	297.119	220.923	−14.425
900	23.367	199.185	184.127	13.552	294.245	211.571	−12.279
1000	23.348	201.646	185.758	15.888	291.313	202.542	−10.580
1100	23.274	203.869	187.305	18.219	288.309	193.809	−9.203
1200	23.165	205.889	188.771	20.541	285.223	185.354	−8.068
1300	23.040	207.738	190.160	22.852	282.045	177.160	−7.118
1400	22.908	209.441	191.477	25.149	278.769	169.214	−6.313
1500	22.776	211.017	192.728	27.433	275.389	161.506	−5.624
1600	22.648	212.483	193.918	29.705	271.902	154.027	−5.028
1700	22.526	213.852	195.050	31.963	268.302	146.769	−4.510
1800	22.411	215.136	196.131	34.210	247.439	140.441	−4.076
1900	22.304	216.345	197.163	36.446	243.705	134.599	−3.700
2000	22.206	217.487	198.151	38.671	239.961	128.953	−3.368
2100	22.114	218.568	199.098	40.887	236.207	123.495	−3.072
2200	22.030	219.595	200.006	43.094	232.444	118.216	−2.807
2300	21.952	220.572	200.880	45.293	228.674	113.108	−2.569
2400	21.881	221.505	201.720	47.485	224.896	108.165	−2.354
2500	21.815	222.397	202.529	49.670	221.111	103.379	−2.160
2600	21.755	223.251	203.310	51.848	217.320	98.744	−1.984
2700	21.699	224.071	204.064	54.021	213.522	94.256	−1.823
2800	21.648	224.860	204.792	56.188	209.720	89.908	−1.677
2900	21.600	225.618	205.497	58.350	205.913	85.696	−1.544
3000	21.556	226.350	206.180	60.508	202.101	81.616	−1.421
3100	21.516	227.056	206.843	62.662	198.285	77.662	−1.309
3200	21.478	227.739	207.485	64.811	−182.370	79.021	−1.290
3300	21.443	228.399	208.109	66.958	−184.541	87.223	−1.381
3400	21.411	229.039	208.715	69.100	−186.714	95.491	−1.467
3500	21.380	229.659	209.305	71.240	−188.889	103.823	−1.549
3600	21.352	230.261	209.878	73.376	−191.069	112.217	−1.628
3700	21.326	230.845	210.437	75.510	−193.252	120.671	−1.704
3800	21.301	231.414	210.982	77.642	−195.440	129.185	−1.776
3900	21.278	231.967	211.513	79.770	−197.633	137.756	−1.845
4000	21.257	232.505	212.031	81.897	−199.833	146.384	−1.912
4100	21.237	233.030	212.537	84.022	−202.039	155.067	−1.976
4200	21.218	233.541	213.031	86.145	−204.253	163.803	−2.037
4300	21.200	234.040	213.513	88.265	−206.475	172.593	−2.097
4400	21.183	234.528	213.986	90.385	−208.707	181.434	−2.154
4500	21.167	235.003	214.447	92.502	−210.948	190.326	−2.209
4600	21.152	235.468	214.899	94.618	−213.201	199.268	−2.263
4700	21.138	235.923	215.342	96.733	−215.465	208.259	−2.315
4800	21.125	236.368	215.775	98.846	−217.742	217.299	−2.365
4900	21.113	236.804	216.200	100.958	−220.033	226.386	−2.413
5000	21.101	237.230	216.616	103.068	−222.339	235.520	−2.460
5100	21.090	237.648	217.025	105.178	−224.661	244.700	−2.506
5200	21.079	238.057	217.425	107.286	−227.000	253.926	−2.551
5300	21.069	238.459	217.818	109.394	−229.357	263.197	−2.594
5400	21.059	238.852	218.204	111.500	−231.733	272.513	−2.636
5500	21.050	239.239	218.583	113.606	−234.129	281.873	−2.677
5600	21.041	239.618	218.955	115.710	−236.548	291.276	−2.717
5700	21.033	239.990	219.321	117.814	−238.990	300.723	−2.756
5800	21.025	240.356	219.681	119.917	−241.456	310.213	−2.794
5900	21.018	240.715	220.034	122.019	−243.948	319.746	−2.831
6000	21.010	241.068	220.382	124.120	−246.467	329.322	−2.867

PREVIOUS: CURRENT: June 1984 (1 bar)

$S°(298.15\ K) = 52.992 \pm 0.4\ J·K^{-1}·mol^{-1}$
$T_{trs} = 652 \pm 3\ K$
$T_{fus} = 1249 \pm 3\ K$

$\Delta_f H°(0\ K) = -87.13 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -87.86 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 6.443 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 30.125 \pm 2.9\ kJ·mol^{-1}$

Enthalpy of Formation

Rosenqvist[1] studied the sulfur vapor pressure above solid nickel sulfides using the N_2/H_2S equilibrium. Combining his data for several equilibria we calculate 2nd and 3rd law values of $\Delta_f H°(298.15\ K)$ for NiS(cr) to be 20.5 ± 0.7 kcal·mol^{-1} and -22.6 ± 3.6 kcal·mol^{-1}, respectively. The stoichiometry of NiS varies from at least $NiS_{.98}$ to $NiS_{1.05}$ and Ariya *et al.*[2] investigated $\Delta_f H°(298.15\ K)$ in the composition range by calorimetric methods. These authors found $\Delta_f H°(298.15\ K) = -20.3 \pm 0.6$ kcal·mol^{-1} for stoichiometric NiS with an ill-defined trend toward more exothermic values at higher sulfur content. DeRanter and Breckpot[3] obtained a value of 20.08 kcal·mol^{-1} for amorphous $Ni_{.98}S$ from an enthalpometric titration. We calculate $\Delta_f H°(298.15\ K) = -21.3$ kcal·mol^{-1} for the same material based on a 3rd law analysis of DeRanter and Breckpot's emf data.[3]

In view of the rather large uncertainties and variations due to stoichiometry we choose to adopt the average of the five values above, $\Delta_f H°(298.15\ K) = -21.0 \pm 1.5$ kcal·mol^{-1}. This value is somewhat less negative than values of -22.1 and -22.5 kcal·mol^{-1} adopted by Mah and Pankrantz[4] and Mills,[5] respectively.

Heat Capacity and Entropy

The low temperature heat capacity data (52–296 K) are taken from Weller and Kelley.[6] High temperature enthalpies of $NiS_{1.03}$ were measured by Conard *et al.*[7] via drop calorimetry. We have joined these values smoothly with the low temperature $C_p°$ measurements of Weller and Kelley[6] to derive the $C_p°$ values from 298 652 K. Values of $C_p°$ above the transition are also taken from our analysis of Conard's *et al.*[7] enthalpy data, disregarding the points above 1000 K to avoid problems due to incongruent melting. Values above 1000 K are extrapolated.

Phase Data

Both the low (β) and high (α) temperature polymorphs of NiS dissolve excess sulfur to form solid solutions. The β phase shows a limited range of homogeneity but the α phase shows a broad limit extending to approximately $NiS_{1.10}$.[8] The α phase is normally designated α $Ni_{1-x}S$ to emphasize this feature. However, the sulfur-poor limit of this phase has the stoichiometric composition to at least 873 K; at 1070 K the deviation from stoichiometry is less than 0.05 weight % nickel.[8] Above 1079 K the deviation of the sulfur-poor limit from stoichiometry increases more rapidly and a material of stoichiometry NiS will exist as an equilibrium mixture of liquid Ni_yS_z and solid α $Ni_{1-x}S$.[8] Thus, NiS melts incongruently.

Transition Data

We adopt 652 ± 3 K as the transition temperature of stoichiometric NiS from rhombohedral (β) to hexagonal (α) form base on the phase diagram of Kullerud and Yund.[8] The temperature of this transition is very dependent on the exact stoichiometry of the material.[8] The transition enthalpy has been measured via a DTA technique by Conard *et al.*[7] and we adopt their value of 1.54 ± 0.1 kcal·mol^{-1}. This is considerably higher than an older value of 0.63 kcal·mol^{-1} measured by Biltz *et al.*[9,5] but should be much more accuiuccirclrate due to the calibration technique used. Mah and Pankrantz[4] estimated 0.7 kcal·mol^{-1}. This transition enthalpy cannot be measured by drop calorimetry since the α form does not revert to the β form on cooling.

Fusion Data

As stated above, stoichiometric NiS will begin to form a liquid at 1079 K. The conversion to stoichiometric liquid NiS is complete at 1249 K.[8] We adopt the latter as the melting point of NiS with an uncertainty estimated to be ±3 K. The adopted heat of melting, $\Delta_{fus} H° = 7.20 \pm 0.7$ kcal·mol^{-1}, is from our analysis of the high temperature enthalpy data of Conard *et al.*[7] This value compares favorably with estimated values of 7.4 and 7.0 kcal·mol^{-1} due to Nagamori and Ingraham[10] and Mah and Pankrantz.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.465	−87.131	−87.131	INFINITE
100	23.187	12.857	89.876	−7.702	−87.566	−86.854	45.368
200	40.626	35.370	57.135	−4.353	−87.748	−86.055	22.475
298.15	47.112	52.992	52.992	0.	−87.864	−85.200	14.927
300	47.196	53.284	52.993	0.087	−87.867	−85.184	14.832
400	50.501	67.332	54.886	4.978	−90.301	−84.172	10.992
500	53.053	78.880	58.563	10.158	−92.016	−82.453	8.614
600	55.312	88.757	62.792	15.579	−93.458	−80.402	7.000
652.000	56.372	93.399	65.050	18.483	BETA <--> ALPHA TRANSITION		
652.000	53.152	103.281	65.050	24.927			
700	54.518	107.105	67.804	27.511	−88.196	−78.598	5.865
800	57.363	114.570	73.189	33.105	−88.900	−77.175	5.039
900	60.208	121.491	78.176	38.983	−142.408	−74.603	4.330
1000	63.053	127.982	82.835	45.146	−141.290	−67.127	3.506
1100	65.898	134.125	87.221	51.594	−139.971	−59.773	2.838
1200	68.743	139.980	91.375	58.326	−138.456	−52.547	2.287
1249.000	70.137	142.759	93.337	61.728	---- ALPHA <--> LIQUID ----		
1300	71.588	145.595	95.332	65.342	−136.751	−45.456	1.826
1400	74.433	151.005	99.116	72.644	−134.864	−38.503	1.437
1500	77.278	156.237	102.751	80.229	−132.797	−31.691	1.104
1600	80.124	161.315	106.253	88.099	−130.554	−25.023	0.817
1700	82.969	166.258	109.638	96.254	−128.142	−18.500	0.568

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = [72.441]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1249 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-62.474]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 30.125 \pm 2.9\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from that of NiS(cr) by adding $\Delta_{fus} H°$ and the difference in enthalpy, H°(1249 K)–H°(298.15 K), between the crystal and liquid. Our 2nd and 3rd law analyses of Nagamori and Ingraham's[1] sulfur vapor pressure data yields $\Delta_f H°(298.15\ K) = 14.4 \pm 0.4$ and $16.7 \pm 0.4\ kcal·mol^{-1}$, respectively. These values agree with the adopted value within the estimated uncertainty. Meyer *et al.*[2] and Rosenqvist[3] conducted similar vapor pressure studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori at overlapping temperatures.[2] However, Meyer's data are presented graphically only and Rosenqvist's data cover only compositions near Ni_3S_2(l) and is not of high enough quality to extrapolate to the proper composition.

Heat Capacity and Entropy

The heat capacity of liquid NiS above an assumed glass transition at 860 K is taken from our analysis of the enthalpy data of Conard *et al.*[4] This value has a fairly high uncertainty because of the limited temperature range of the data (35 K). It is in reasonable agreement with the estimated $C_p° = 17\ cal\ K^{-1}·mol^{-1}$ of Mah and Pankrantz.[5] The heat capacity below the glass transition is that of the crystal. $S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

The Gibbs energy data indicates that NiS(l) will decompose to the elements, Ni(l) + 1/2 S_2(g), at a temperature of 2350 ± 200 K and a fugacity of 1 atm. In view of the uncertainty in the Gibbs free energy data, computation of the exact zero point does not seem justified. Since the Gibbs energy data for NiS(l) and NiS(g)[6] intersect at 2990 ± 220 K, it seems clear that decomposition will occur rather than boiling.

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[5]A. D. Mah and L. B. Pankrantz, U. S. Bur. Mines Bull. 668, 125 pp. (1976).
[6]JANAF Thermochemical Tables: NiS(g), 12–31–76.

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	47.112	72.441	72.441	0.	−62.474	−65.609	11.494
300	47.196	72.732	72.442	0.087	−62.477	−65.629	11.427
400	50.501	86.780	74.334	4.978	−64.911	−66.561	8.692
500	53.053	98.329	78.012	10.158	−66.627	−66.788	6.977
600	55.312	108.206	82.240	15.579	−68.069	−66.681	5.805
652.000	56.372	112.847	84.498	18.483	BETA <--> ALPHA		
652.000	53.152	122.729	84.498	24.927	TRANSITION		
700	54.518	126.553	87.252	27.511	−62.807	−66.823	4.986
800	57.363	134.019	92.638	33.105	−63.511	−67.344	4.397
860.000	59.070	138.228	95.673	36.598	GLASS <--> LIQUID		
860.000	76.776	138.228	95.673	36.598	TRANSITION		
900	76.776	141.719	97.642	39.669	−116.333	−66.733	3 873
1000	76.776	149.808	102.461	47.346	−113.701	−61.363	3.205
1100	76.776	157.125	107.103	55.024	−111.151	−56.254	2.671
1200	76.776	163.806	111.554	62.702	−108.690	−51.372	2.236
1249 000	76.776	166.878	113.665	66.464	ALPHA <--> LIQUID		
1300	76.776	169.951	115.813	70.379	−106.325	−46.692	1.876
1400	76.776	175.641	119.886	78.057	−104.061	−42.191	1.574
1500	76.776	180.938	123.781	85.735	−101.902	−37.847	1.318
1600	76.776	185.893	127.510	93.412	−99.852	−33.645	1.098
1700	76.776	190.547	131.083	101.090	−97.916	−29.567	0.908
1800	76.776	194.936	134.509	108.768	−113.247	−24.884	0.722
1900	76.776	199.087	137.800	116.445	−111.450	−20.024	0.551
2000	76.776	203.025	140.964	124.123	−109.664	−15.259	0.399
2100	76.776	206.771	144.009	131.800	−107.890	−10.582	0.263
2200	76.776	210.343	146.944	139.478	−106.126	−5.990	0.142
2300	76.776	213.755	149.775	147.156	−104.372	−1.477	0.034
2400	76.776	217.023	152.509	154.833	−102.626	2.959	−0.064
2500	76.776	220.157	155.153	162.511	−100.888	7.322	−0.153
2600	76.776	223.168	157.711	170.189	−99.158	11.617	−0.233
2700	76.776	226.066	160.190	177.866	−97.433	15.845	−0.307
2800	76.776	228.858	162.593	185.544	−95.714	20.009	−0.373
2900	76.776	231.552	164.924	193.222	−94.001	24.111	−0.434
3000	76.776	234.155	167.189	200.899	−92.294	28.155	−0.490
3100	76.776	236.673	169.390	208.577	−90.590	32.142	−0.542
3200	76.776	239.110	171.531	216.254	−465.726	41.262	−0.674
3300	76.776	241.473	173.615	223.932	−462.379	57.054	−0.903
3400	76.776	243.765	175.644	231.610	−459.034	72.744	−1.118

PREVIOUS: CURRENT: December 1976

CRYSTAL(β-α)–LIQUID

0 to 652 K crystal, rhombohedral (β)
652 to 1249 K crystal, hexagonal (α)
above 1249 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−8.465	−87.131	−87.131	INFINITE
100	23.187	12.857	89.876	−7.702	−87.566	−86.854	45.368
200	40.626	35.370	57.135	−4.353	−87.748	−86.055	22.475
298.15	47.112	52.992	52.992	0.	−87.864	−85.200	14.927
300	47.196	53.284	52.993	0.087	−87.867	−85.184	14.832
400	50.501	67.332	54.886	4.978	−90.301	−84.172	10.992
500	53.053	78.880	58.563	10.158	−92.016	−82.453	8.614
600	55.312	88.757	62.792	15.579	−93.458	−80.402	7.000
652.000	56.372	93.399	65.050	18.483	BETA <--> ALPHA		
652.000	53.152	103.281	65.050	24.927	TRANSITION		
700	54.518	107.105	67.804	27.511	−88.196	−78.598	5.865
800	57.363	114.570	73.189	33.105	−88.900	−77.175	5.039
900	60.208	121.491	78.176	38.983	−142.408	−74.603	4.330
1000	63.053	127.982	82.835	45.146	−141.290	−67.127	3.506
1100	65.898	134.125	87.221	51.594	−139.971	−59.773	2.838
1200	68 743	139.980	91.375	58.326	−138.456	−52.547	2.287
1249.000	70.137	142.759	93.337	61.728	ALPHA <--> LIQUID		
1249.000	76.776	166.878	93.337	91.853	TRANSITION		
1300	76.776	169.951	96.283	95.769	−106.325	−46.692	1.876
1400	76.776	175.641	101.751	103.447	−104.061	−42.191	1.574
1500	76.776	180.938	106.855	111.124	−101.902	−37.848	1.318
1600	76.776	185.893	111.642	118.802	−99.852	−33.645	1.098
1700	76.776	190.547	116.148	126.479	−97.916	−29.567	0.908
1800	76.776	194.936	120.404	134.157	−113.247	−24.884	0.722
1900	76.776	199.087	124.437	141.835	−111.450	−20.024	0.551
2000	76.776	203.025	128.269	149.512	−109.664	−15.259	0.399
2100	76.776	206.771	131.919	157.190	−107.890	−10.582	0.263
2200	76.776	210.343	135.403	164.868	−106.126	−5.990	0.142
2300	76.776	213.756	138.736	172.545	−104.372	−1.477	0.034
2400	76.776	217.023	141.930	180.223	−102.626	2.959	−0.064
2500	76.776	220.157	144.997	187.901	−100.888	7.322	−0.153
2600	76.776	223.168	147.946	195.578	−99.158	11.617	−0.233
2700	76.776	226.066	150.786	203.256	−97.433	15.845	−0.307
2800	76.776	228.858	153.525	210.933	−95.714	20.008	−0.373
2900	76.776	231.552	156.169	218.611	−94.001	24.111	−0.434
3000	76.776	234.155	158.726	226.289	−92.294	28.155	−0.490
3100	76.776	236 673	161.200	233.966	−90.590	32.142	−0.542
3200	76.776	239.110	163.597	241.644	−465.726	41.262	−0.674
3300	76.776	241.473	165.921	249.322	−462.379	57.054	−0.903
3400	76.776	243.765	168.177	256.999	−459.034	72.744	−1.118

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = [252.282 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 357.40 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 357.42 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
[0]	[9]
[1360.7]	[7]
[2269.6]	[5]
[16661.6]	[5]
[16977.8]	[3]
[17230.7]	[1]

$\omega_e = 544\ cm^{-1}$ $\omega_e x_e = 2.6\ cm^{-1}$ $\sigma = 1$
$B_e = [0.191]\ cm^{-1}$ $\alpha_e = [0.0011]\ cm^{-1}$ $r_e = [2.07]$ Å

Enthalpy of Formation

Drowart *et al.*[1] used a modified Knudsen cell and a mass spectrometric technique to study the equilibrium NiS(g) + Mn(g) = MnS(g) + Ni(g). Since they report no data, we adopt their value of $D_0° = 81.5 \pm 3.5$ kcal·mol^{-1} based on their 3rd law analysis of this equilibrium. With auxiliary JANAF data[2] this yields $\Delta_f H°(298.15\ K) = 85.4 \pm 4.0$ kcal·mol^{-1}. Trevedi[3] studied the absorption spectrum of NiS and determined $D_0° = 101.6$ kcal·mol^{-1} from the onset of continuous absorption due to photodissociation. This value is likely to be too high in view of the experimental difficulties in determining the exact position of the onset of continuous absorption. Complications arise because of background emission from the furnace. A Birge–Sponer extrapolation of the vibrational data to determine $D_0°$ is not meaningful since DeVore and Franzen[4] used the reverse procedure to arrive at the reported value of $\omega_e x_e$.

Heat Capacity and Entropy

No experimental information is available on the electronic structure of NiS. The electronic states are estimated to be identical to those of the Ni^{2+} ion[5] following the procedure of Brewer and Rosenblatt[6] for the transition metal oxides. As stated by Brewer and Robenblatt,[6] this procedure usually overestimates the contribution of electronic states. Nevertheless, it appears to be the best method available. The uncertainty assigned to $S°(298.15\ K)$ is based mainly on the uncertainties in this approximation since the presence of the sulfide ion will undoubtedly alter the electronic structure of the nickel ion. Levels above 50,000 cm^{-1} are not included since they have a negligible effect on the thermodynamic properties. The vibrational constants are taken from a study of the matrix isolation spectrum by DeVore and Franzen.[4] The rotational constants are estimated based on an oxide–sulfide correlation due to Barrow and Cousins,[7] $r(NiS) = 0.237 + 1.116\ r(NiO)$. The value $r(NiO) = 1.64$ Å is taken from Brewer and Chandraskharaiah.[8] The value of α_e is estimated assuming a Morse potential function using the expression given by Herzberg.[9]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.218	357.398	357.398	INFINITE
100	29.323	218.044	281.104	−6.306	359.113	339.306	−177.235
200	31.871	239.056	255.355	−3.260	358.628	319.584	−83.467
250	33.262	246.320	252.843	−1.631	358.063	309.886	−64.747
298.15	34.452	252.282	252.282	0.	357.419	300.664	−52.675
300	34.495	252.496	252.283	0.064	357.392	300.312	−52.289
350	35.599	257.897	252.707	1.817	356.646	290.857	−43.408
400	36.597	262.717	253.663	3.622	353.625	281.600	−36.773
450	37.497	267.081	254.915	5.475	352.101	272.680	−31.652
500	38.297	271.074	256.334	7.370	350.478	263.944	−27.574
600	39.598	278.177	259.397	11.268	347.513	246.918	−21.496
700	40.520	284.355	262.531	15.277	344.853	230.375	−17.191
800	41.118	289.808	265.607	19.361	342.639	214.174	−13.984
900	41.463	294.673	268.571	23.492	287.384	199.325	−11.569
1000	41.624	299.051	271 404	27.648	286.494	189.588	−9.903
1100	41.658	303.021	274.100	31.813	285.530	179.943	−8.545
1200	41.608	306.644	276.664	35.977	284.477	170.390	−7.417
1300	41.507	309.971	279.099	40 133	283.321	160.929	−6.466
1400	41.377	313.042	281.416	44.277	282.052	151.561	−5.655
1500	41.234	315.892	283.620	48.408	280.664	142.287	−4.955
1600	41.087	318.549	285.721	52.524	279.153	133.111	−4.346
1700	40.944	321.035	287.726	56.625	277.512	124.033	−3.811
1800	40.807	323.371	289.642	60.713	258.592	115 770	−3.360
1900	40.679	325.574	291.476	64.787	256.785	107.885	−2.966
2000	40.562	327.658	293.233	68.849	254.955	100.095	−2.614
2100	40 456	329.634	294.920	72.900	253.102	92.397	−2.298
2200	40.362	331.514	296.541	76.940	251.229	84 789	−2.013
2300	40.278	333.306	298.101	80.972	249.338	77.265	−1.755
2400	40.206	335.019	299 604	84.996	247.430	69.825	−1.520
2500	40.144	336.659	301.053	89 014	245.508	62.464	−1.305
2600	40.092	338.232	302.453	93.026	243.572	55 181	−1.109
2700	40.049	339.745	303.807	97.032	241.626	47.972	−0.928
2800	40.015	341.200	305.116	101.036	239.670	40.835	−0.762
2900	39.990	342.604	306.385	105.036	237.706	33.768	−0.608
3000	39.973	343.960	307.615	109.034	235.734	26 770	−0.466
3100	39.963	345.270	308.809	113.031	233.756	19.837	−0.334
3200	39.961	346.539	309.968	117.027	−145.061	18.156	−0.296
3300	39.964	347.769	311.095	121.023	−145.395	23.262	−0.368
3400	39.974	348.962	312.191	125.020	−145.731	28.378	−0.436
3500	39.990	350.121	313.258	129.018	−146.070	33.504	−0.500
3600	40.011	351.248	314.298	133.018	−146.411	38.639	−0.561
3700	40.036	352.344	315.312	137.020	−146.756	43.784	−0.618
3800	40.066	353.412	316.300	141.025	−147.105	48.938	−0.673
3900	40.100	354.453	317.265	145.034	−147.457	54.102	−0.725
4000	40.138	355.469	318.208	149.046	−147.815	59.275	−0.774
4100	40.178	356.461	319.129	153.061	−148.178	64 457	−0.821
4200	40.222	357.429	320.029	157.081	−148.547	69.647	−0.866
4300	40.269	358.376	320.910	161.106	−148.923	74.847	−0.909
4400	40.318	359.303	321.772	165.135	−149.308	80.055	−0.950
4500	40.369	360.209	322.616	169.169	−149.701	85.272	−0.990
4600	40 422	361.097	323.443	173.209	−150.104	90.498	−1.028
4700	40.476	361.967	324.253	177.254	−150.518	95.733	−1.064
4800	40.532	362.820	325.048	181.304	−150.944	100.977	−1.099
4900	40.589	363.656	325.828	185.360	−151.384	106.230	−1.132
5000	40.647	364 477	326.592	189.422	−151.838	111.492	−1.165
5100	40.706	365.282	327.343	193.490	−152.307	116.763	−1.196
5200	40.765	366.073	328.080	197.563	−152.793	122.044	−1.226
5300	40.825	366.850	328.804	201.643	−153.298	127.334	−1.255
5400	40.886	367.614	329.516	205.728	−153.822	132.634	−1.283
5500	40.946	368.365	330.216	209.820	−154.366	137.943	−1.310
5600	41.007	369 103	330.904	213.918	−154.933	143.263	−1.336
5700	41.067	369.829	331.580	218.021	−155.524	148.593	−1.362
5800	41.128	370.544	332.246	222.131	−156.139	153.934	−1.386
5900	41.188	371.248	332.901	226.247	−156.781	159.286	−1.410
6000	41.249	371.941	333.546	230.369	−157.451	164.648	−1.433

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K)$ = [71.965 ± 8.4] J·K^{-1}·mol^{-1}
T_{fus} = 1280 ± 5 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −131.38 ± 16.7 kJ·mol^{-1}
$\Delta_{fus} H°$ = [65.689 ± 8.4] kJ·mol^{-1}

Enthalpy of Formation

Our analysis of equilibrium data involving NiS_2 is summarized below.

Source	Reaction*	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
[1]	A	298.15	1	calorimetric	−35.1	
[2]	B	923–1033	5	−46.3 ± 0.4	−47.1 ± 0.1	−0.8 ± 0.4
[3]	B	673–873	equation	−49.2	−48.7	0.7
[4]	C	500–723	2	13.9	−5.1 ± 9.9	−31.4
[5]	C	673–873	20	−2.9 ± 0.2	−7.5 ± 2.4	−14.1 ± 0.3
[6]	A	298.15	1	emf[$\Delta G°(298.15\ K) = -24.3$)]	−25.9	

*A) Ni(cr) + 2 S(cr) = NiS_2(cr)
B) 2 $Ni_{1-x}S$(cr) + S_2(g) = 2 NiS_2(cr)
C) $Ni_{1-x}S$(cr) + H_2S(g) = NiS_2(cr) + H_2(g)

The studies due to Delafosse and Barret[4] and Rosenqvist[5] show poor agreement between 2nd and 3rd law values of $\Delta_r H°$ as well as a large 3rd law drift and are not considered further. Kullerud and Yund[7] mention that a coating of NiS_2(cr) often forms on $Ni_{1-x}S$(cr) and it seems possible that this may lead to a slow establishment of equilibrium in this system. DeRanter and Breckpot[6] state that their results may be biased for NiS_2(cr) since it is a semiconductor and this may interfere in emf measurements. Consequently their results are not considered further. 3rd law results of Biltz *et al.*[2] and Leegaard and Rosenquist[3] yield values of $\Delta_f H°(298.15\ K)$ = −29.1 ± 1.6 and −29.8 ± 1.7 kcal·mol^{-1}, respectively, when combined with auxiliary JANAF data.[8] These values are averaged with the calorimetric value due to Ariya[1] of −35.1 kcal·mol^{-1} to yield the adopted value of −31.4 kcal·mol^{-1}. An uncertainty of ±4 kcal·mol^{-1} is assigned due mainly to the variation in stoichiometry of one of the reactants, $Ni_{1-x}S$. The adopted value compares favorably with a value of −32.0 kcal·mol^{-1} obtained by Mills[9] in a recent critical evaluation. It also compares favorably with a value of −31.3 kcal·mol^{-1} calculated assuming the same contribution per gram-atom as in NiS and Ni_3S_2.[8]

Heat Capacity and Entropy

The only heat capacity measurements on NiS_2 are those of Winterberger and Bonnerot[10] at low temperature (5–10 K). Consequently the heat capacity is estimated via the following procedure. The value at 298.15 K is estimated assuming the same contribution per gram-atom as in NiS and Ni_3S_2[8] yielding $C_p°(298.15\ K)$ = 16.88 cal·K^{-1}·mol^{-1}. The temperature dependence is estimated using method A of Kubaschewski *et al.*[11] This yields $C_p° = 15.401 + 4.960 \times 10^{-3}\ T$.

2nd law analyses of equilibrium data of Leegaard and Rosenqvist[3] and Biltz *et al.*[2] combined with auxiliary JANAF data[8] yield $S°(298.15\ K)$ = 16.89 and 17.60 cal·K^{-1}·mol^{-1}, respectively. We adopt the average of these values, 17.2 cal·K^{-1}·mol^{-1}, with an uncertainty estimated to be ±2 cal K^{-1}·mol^{-1}. Similar analyses of studies of Delafosse and Barret[4] and Rosenqvist[5] give values of 13.10 and 29.96 cal·K^{-1}·mol^{-1}, respectively, but as mentioned above, these studies do not appear to be reliable since equilibrium may not have been established. A value of 19.10 cal·K^{-1}·mol^{-1} is obtained assuming the same contribution per gram-atom as in NiS and Ni_3S_2.[8] This is somewhat higher than the adopted value but this may be reasonable since the crystal symmetry of NiS_2 is higher (cubic) than that of NiS and Ni_3S_2 (hexagonal).[7]

Fusion Data

The melting point of NiS_2(cr) is taken from the phase study by Kullerud and Yund.[7] The enthalpy of melting of NiS_2 is unknown and is estimated as follows. Lewis and Randall[12] point out that the sum of the entropy of transition(s) plus the entropy of fusion is approximately constant, on a gram-atom basis, for compounds of similar structure. Using NiS and Ni_3S_2[8] as base compounds, we calculate the above sums to be 4.06 and 4.13 cal·K^{-1} g-atom^{-1}, respectively. Since NiS_2 has no known transition, we use the average value of 4.10 cal·K^{-1}·g-atom^{-1} to calculate $\Delta_{fus}S°(NiS_2)$ = 12.3 cal·K^{-1}·mol^{-1} which yields $\Delta_{fus}H°$ = 15.7 kcal·mol^{-1} with an estimated uncertainty of ±2.0 kcal·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
250							
298.15	70.626	71.965	71.965	0.	−131.378	−124.813	21.867
300	70.664	72.402	71.966	0.131	−131.379	−124.772	21.725
400	72.739	93.015	74.763	7.301	−136.131	−122.358	15.978
500	74.814	109.469	80.112	14.678	−139.577	−118.542	12.384
600	76.889	123.292	86.186	22.264	−142.439	−114.057	9.930
700	78.965	135.301	92.363	30.056	−144.663	−109.134	8.144
800	81.040	145.981	98.410	38.057	−146.172	−103.951	6.787
900	83.115	155.646	104.241	46.264	−253.607	−96.438	5.597
1000	85.190	164.510	109.830	54.680	−252.093	−79.055	4.129
1100	87.266	172.727	115.179	63.302	−250.470	−61.829	2.936
1200	89.341	180.409	120.298	72.133	−248.744	−44.755	1.948
1280.000	91.001	186.228	124.238	79.346	--- CRYSTAL <---> LIQUID ---		
1300	91.416	187.642	125.203	81.171	−246.921	−27.829	1.118
1400	93.491	194.493	129.910	90.416	−245.007	−11.047	0.412
1500	95.567	201.014	134.434	99.869	−243.006	5.595	−0.195
1600	97.642	207.248	138.792	109.529	−240.921	22.101	−0.722
1700	99.717	213.229	142.996	119.397	−238.758	38.474	−1.182
1800	101.793	218.988	147.058	129.473	−253.667	55.432	−1.609

PREVIOUS: CURRENT: March 1977

$S°(298.15\ K) = [122.427]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1280 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-66.568]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [65.689 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

There are no experimental studies of the enthalpy of formation of NiS_2(l). Therefore, $\Delta_f H°(NiS_2, l, 298.15\ K)$ is calculated from that of NiS_2(cr)[1] by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1280\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to remain constant at 21.75 $cal·K^{-1}·mol^{-1}$ (the value of NiS_2(cr) at the melting point) above an assumed glass transition point of 960 K. Below that temperature the crystal heat capacity[1] is assumed to be valid.

$S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

Under standard conditions (1 atm. pressure) the use of auxiliary JANAF data[1] indicates that NiS_2(l) will decompose spontaneously to NiS(l) + 1/2 S_2(g) at all temperatures above the normal melting point. This appears to be at variance with the phase diagram of Kullerud and Yund[2] which indicates the presence of a liquid of variable composition in the Ni S system from a stoichiometry less than Ni_3S_2 to just above NiS_2 at temperatures slightly above the melting point. However, the authors point out that this diagram does not refer to a constant pressure system and give a short discussion of the loss of sulfur to the vapor from NiS_2(cr). From the sealed tube experiments of Kullerud and Yund[2] it does appear that NiS_2(l) will be stable under its own vapor pressure in a sealed tube.

References

[1]JANAF Thermochemical Tables: NiS_2(cr), 3-31-77; NiS(l), 12-31-76; S_2(g), 12-31-65.
[2]G. Kullerud and R. A. Yund, J. Petrology 3, 126 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	70.626	122.427	122.427	0.	−66.568	−75.048	13.148
300	70.664	122.864	122.428	0.131	−66.569	−75.101	13.076
400	72.739	143.477	125.225	7.301	−71.321	−77.733	10.151
500	74.814	159.931	130.574	14.678	−74.767	−78.963	8.249
600	76.889	173.754	136.648	22.264	−77.629	−79.524	6.923
700	78.965	185.763	142.825	30.056	−79.853	−79.647	5.943
800	81.040	196.443	148.872	38.057	−81.362	−79.511	5.192
900	83 115	206.108	154.703	46.264	−188.797	−77.044	4.471
960.000	84.360	211.511	158.086	51.289	GLASS <--> LIQUID		
960.000	91.002	211.511	158.086	51.289	TRANSITION		
1000	91.002	215.226	160.298	54.929	−187.034	−64.712	3.380
1100	91.002	223.900	165.692	64.029	−184.934	−52.582	2.497
1200	91.002	231.818	170.877	73.129	−182.937	−40.639	1.769
1280.000	91.002	237.691	174.871	80.409	--- CRYSTAL <--> LIQUID ---		
1300	91.002	239 102	175.849	82.229	−181.052	−28.858	1.160
1400	91.002	245.846	180.611	91.329	−179.283	−17.218	0.642
1500	91.002	252.124	185.171	100.430	−177.635	−5.700	0.199
1600	91.002	257.998	189.541	109.530	−176.111	5.712	−0.186
1700	91.002	263.515	193.732	118.630	−174.715	17.032	−0.523
1800	91.002	268.716	197.755	127.730	−190.600	28.989	−0.841

PREVIOUS: CURRENT: March 1977

0 to 1280 K crystal
above 1280 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
250							
298.15	70.626	71.965	71.965	0.	−131.378	−124.813	21.867
300	70.664	72.402	71.966	0.131	−131.379	−124.772	21.725
400	72.739	93.015	74.763	7.301	−136.131	−122.358	15.978
500	74.814	109.469	80.112	14.678	−139.577	−118.542	12.384
600	76.889	123.292	86.186	22.264	−142.439	−114.057	9.930
700	78.965	135.301	92.363	30.056	−144.663	−109.134	8.144
800	81.040	145.981	98.410	38.057	−146.172	−103.951	6.787
900	83.115	155.646	104.241	46.264	−253.607	−96.438	5.597
1000	85.190	164.510	109.830	54.680	−252.093	−79.055	4.129
1100	87.266	172.727	115.179	63.302	−250.470	−61.829	2.936
1200	89.341	180.409	120.298	72.133	−248.744	−44.755	1.948
1280.000	91.001	186.228	124.238	79.346	CRYSTAL <--> LIQUID TRANSITION		
1280.000	91.002	237.691	124.238	145.219			
1300	91.002	239.102	125.995	147.039	−181.052	−28.858	1.160
1400	91.002	245.846	134.318	156.140	−179.283	−17.218	0.642
1500	91.002	252.124	141.965	165.240	−177.635	−5.700	0.199
1600	91.002	257.998	149.035	174.340	−176.111	5.712	−0.186
1700	91.002	263.515	155.609	183.440	−174.715	17.032	−0.523
1800	91.002	268.716	161.749	192.540	−190.600	28.989	−0.841

PREVIOUS: CURRENT: March 1977

$S°(298.15\ K) = 133.887 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 829 \pm 3\ K$
$T_{fus} = 1062 \pm 3\ K$

$\Delta_f H°(0\ K) = -214.29 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -216.31 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 56.233 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.748 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Three sets of authors studied the phase equilibrium between Ni_3S_2(cr) and Ni(cr) by use of the $H_2(g)/H_2S(g)$ method.[1,2,3] Our 3rd law analyses of the data due to Rosenqvist,[1] Sudo[2] and Line and Laffitte[3] yield $\Delta_f H°(298.15\ K) = -51.6 \pm 1.0$, -50.1 ± 1.6, and -53.4 ± 1.8 $kcal \cdot mol^{-1}$, respectively. We adopt the average of the values, $\Delta_f H°(298.15\ K) = -51.7 \pm 1.7\ kcal \cdot mol^{-1}$. Ariya *et al.*[4] and Vanyukov and Kiseleva[5] reported calorimetric values of -48.3 ± 0.9 and $-43.3\ kcal \cdot mol^{-1}$, respectively. Vanuykov's value is undoubtedly incorrect since Mills[6] determined that values for Fes and MnS from the same study are approximately 25% too low. A 3rd law analysis of the emf value reported by DeRanter and Breckpot[7] yields $\Delta_f H°(298.15\ K) = -38.7\ kcal \cdot mol^{-1}$. This value, however, refers to an amorphous material. At least part of the variation in values of the enthalpy of formation apparently is a result of the very wide range of stoichiometry for the high temperature phase of Ni_3S_2.[8,9]

Heat Capacity and Entropy

The low temperature heat capacities (52–296 K) are from Weller and Kelley.[10] The high heat capacities are from our analysis of the high temperature enthalpy (298 15–1050 K) data of Conard *et al.*[11] Our analysis differs slightly from that of Conard *et al.*[11] since we have forced the high and low temperature heat capacities to join smoothly at 298.15 K. Data above 1050 K are extrapolated assuming a constant heat capacity for the hugh temperature phase of Ni_3S_2. The thermodynamic functions show good agreement with those reported by Mah and Pankrantz.[12]

The entropy at 298.15 is calculated based on an extrapolation of $S°(51\ K) = 2.06\ cal \cdot K^{-1} \cdot mol^{-1}$ by Weller and Kelley.[10]

Phase Data

A phase transition is observed at 829 K for Ni_3S_2.[8] Below the transition, Kullerud and Yund[8] reported the material to be stoichiometric within the limits of ±0.3 weight percent while Rau[9] reported the homogeneity range to extend over a smaller range and to the sulfur rich side only. Above the phase transition, a wide range of homogeneity exists for $Ni_{3 \pm x}S_2$ from approximately $Ni_{2.5}S_2$ to $Ni_{3.7}S_2$.[1,8,9] The phase diagram indicates that upon heating stoichiometric Ni_3S_2, a two phase region [Ni_yS_2(l) + $Ni_{3 \pm x}S_2$(cr)] will be encountered within a few degrees of the formation of stoichiometric liquid Ni_3S_2.[8,9]

Transition Data

We adopt a value of 829 ± 3 K for the phase transition from Ni_3S_2 to $Ni_{3 \pm x}S_2$ based on the detailed study by Kullerud and Yund.[8] This value is in fair agreement with values of 838 and 828 ± 5 reported by Rau[9] and Rosenqvist,[1] respectively. The adopted heat of transition is from our analysis of the high temperature enthalpy data of Conard *et al.*[11] Mah and Pankrantz[12] reported the transition at 840 K with $\Delta_f H° = 13.38\ kcal \cdot mol^{-1}$ in excellent agreement with the adopted $\Delta_{trs} H°$.

Fusion Data

Kullerud and Yung[8] reported that stoichiometric Ni_3S_2 begins to melt at 1055 K with melting completed at 1062 K. The cooling curve yielded identical results. In view of the two phase region in the phase diagram, we adopt the latter temperature as the melting point with an estimated uncertainty of ±3 K. The adopted heat of melting is from our analysis of Conard's *et al.* high temperature enthalpy data[11] and is in good agreement with a value of $4.70\ kcal \cdot mol^{-1}$ reported by Mah and Pankrantz.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−21.156	−214.288	−214.288	INFINITE
100	58.116	33.666	225.939	−19.227	−215.261	−213.887	111.723
200	101.489	89.917	144.221	−10.861	−215.847	−212.256	55.436
298.15	117.738	133.887	133.887	0.	−216.313	−210.399	36.861
300	117.947	134.616	133.889	0.218	−216.323	−210.362	36.627
400	127.110	169.857	138.632	12.490	−221.430	−208.103	27.175
500	133.972	198.975	147.871	25.552	−225.126	−204.371	21.350
600	139.913	223.932	158.516	39.249	−228.432	−199.906	17.403
700	145.436	245.918	169.462	53.519	−230.824	−194.922	14.545
800	150.708	265.685	180.275	68.328	−231.697	−189.725	12.388
829.000	152 .190	271.078	183.357	72.720	I <--> II		
829 000	188 .615	338.910	183.357	128.953	TRANSITION		
900	188.615	354.410	196.248	142.345	−279.582	−187.213	10.866
1000	188.615	374.282	213.076	161.206	−274.001	−177.251	9.259
1062 000	188 .615	385.628	222.821	172.901	------- II <--> LIQUID -----		
1100	188.615	392.259	228.561	180.068	−268.653	−167.837	7.970
1200	188.615	408.671	242.896	198.929	−263.555	−158.899	6.917
1300	188.615	423.768	256.236	217.791	−258.727	−150.376	6.042
1400	188.615	437.746	268.708	236.652	−254.188	−142.213	5.306
1500	188.615	450.759	280.416	255.514	−249.949	−134.365	4.679
1600	188.615	462.932	291.447	274.375	−246.023	−126.789	4 139

PREVIOUS: CURRENT: December 1976

$S°$(298.15 K) = [215.930] J·K^{-1}·mol^{-1}
T_{fus} = 1062 ± 3 K

$\Delta_f H°$(298.15 K) = [−143.926] kJ·mol^{-1}
$\Delta_{fus} H°$ = 19.748 ± 0.4 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is derived from that of Ni_3S_2(cr) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(1062 K)–$H°$(298.15 K), between crystal and liquid. Our 2nd and 3rd law analyses of Nagamori and Ingraham's equilibrium data[1] yield $\Delta_f H°$(298.15 K) = −33.7 ± 6 and −33.9 ± 0.3 kcal·mol^{-1}, respectively, in good agreement with the adopted value. Meyer *et al.*[2] and Rosenqvist[3] conducted similar studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori and Ingraham at overlapping temperatures,[2] but Meyer's data are only presented graphically so a re analysis is not feasible. Rosenqvist's study included compositions near, but not exactly at, the Ni_3S_2 stoichiometry. Our extrapolation of his data to the proper stoichiometry leads to a higher value of $K_p°$ at 900 K than at 800 or 1000 K. We conclude that Rosenqvist's data are not of sufficient precision for the small number of points at each temperature (3 or 4) to yield meaningful results when extrapolated.

Heat Capacity and Entropy

The enthalpy of Ni_3S_2(l) from the melting point to 1250 K was measured by Conard *et al.*[4] Our analysis of these data yields the adopted constant heat capacity of 45.84 cal·K^{-1}·mol^{-1}. Above 1250 K the heat capacity is assumed to remain constant. This value is in good agreement with a value of 45.20 cal·K^{-1}·mol^{-1} reported by Mah and Pankrantz.[5]

$S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

There is no evidence for the existence of Ni_3S_2(g). In the absence of such information we can only point out that Ni_3S_2(l) will decompose to the gaseous elements at 3240 ± 15 K according to the Gibbs energy of formation in this table. This seems to yield an excessively long liquid range for Ni_3S_2.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	117.738	215.930	215.930	0.	−143.926	−162.473	28.465
300	117.947	216.659	215.932	0.218	−143.937	−162.588	28.309
400	127.110	251.900	220.675	12.490	−149.043	−168.534	22.008
500	133.972	281.018	229.914	25.552	−152.739	−173.006	18.074
600	139.913	305.975	240.560	39.249	−156.045	−176.745	15.387
700	145.436	327.963	251.505	53.520	−158.436	−179.966	13.429
760.000	148.549	340.051	258.024	62.341	GLASS <--> LIQUID		
760.000	191 .795	340.051	258.024	62.341	TRANSITION		
800	191.795	349.889	262.373	70.012	−157.626	−183.018	11.950
900	191.795	372.479	273.377	89.192	−260.348	−184.242	10.693
1000	191.795	392.686	284.315	108.371	−254.450	−176.104	9.199
1062.000	191.795	404.224	290.982	120.263	----- II <--> LIQUID		-----
1100	191.795	410.966	295.011	127.551	−248.784	−168.546	8.004
1200	191.795	427.655	305.379	146.730	−243.368	−161.493	7.030
1300	191.795	443.006	315.383	165.910	−238.222	−154.880	6.223
1400	191.795	457.220	325.013	185.089	−233.365	−148.654	5.546
1500	191.795	470.452	334.273	204.269	−228.808	−142.764	4.971
1600	191.795	482.830	343.175	223.448	−224.564	−137.168	4.478
1700	191.795	494.458	351.736	242.628	−220.648	−131.827	4.051
1800	191.795	505.421	359.972	261.807	−268.516	−124.563	3.615
1900	191.795	515.790	367.903	280.987	−264.989	−116.662	3.207
2000	191.795	525.628	375.545	300.166	−261.486	−108.946	2.845
2100	191.795	534.986	382.917	319.345	−258.004	−101.404	2.522
2200	191.795	543.908	390.033	338.525	−254.543	−94.028	2.233
2300	191.795	552.434	396.910	357.704	−251.101	−86.809	1.972
2400	191.795	560.596	403.562	376.884	−247.677	−79.740	1.735
2500	191.795	568.426	410.001	396.063	−244.268	−72.812	1.521
2600	191.795	575.948	416.240	415.243	−240.874	−66.021	1.326
2700	191.795	583.187	422.290	434.422	−237.491	−59.360	1.148
2800	191.795	590.162	428.161	453.602	−234.121	−52.825	0.985
2900	191.795	596.892	433.864	472.781	−230.762	−46.409	0.836
3000	191 795	603.394	439.407	491.961	−227.413	−40.109	0.698
3100	191.795	609.683	444.799	511.140	−224.074	−33.921	0.572
3200	191.795	615.772	450.048	530.319	−1351.248	−12.274	0.200
3300	191.795	621.674	455.159	549.499	−1342.966	29.440	−0.466
3400	191.795	627.400	460.141	568.678	−1334.689	70.904	−1.089
3500	191.795	632.959	465.000	587.858	−1326.421	112.125	−1.673
3600	191.795	638.362	469.741	607.037	−1318.162	153.109	−2.222
3700	191.795	643.617	474.370	626.217	−1309.915	193.864	−2.737
3800	191.795	648.732	478.891	645.396	−1301.683	234.397	−3.222

PREVIOUS: CURRENT: December 1976

0	to	829	K crystal, I
829	to	1062	K crystal, II
above		1062	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−21.156	−214.288	−214.288	INFINITE
100	58.116	33.666	225.939	−19.227	−215.261	−213.887	111.723
200	101.489	89.917	144.221	−10.861	−215.847	−212.256	55.436
298.15	117.738	133.887	133.887	0.	−216.313	−210.399	36.861
300	117.947	134.616	133.889	0.218	−216.323	−210.362	36.627
400	127.110	169.857	138.632	12.490	−221.430	−208.103	27.175
500	133.972	198.975	147.871	25.552	−225.126	−204.371	21.350
600	139.913	223.932	158.516	39.249	−228.432	−199.906	17.403
700	145.436	245.918	169.462	53.519	−230.824	−194.922	14.545
800	150.708	265.685	180.275	68.328	−231.697	−189.725	12.388
829.000	152.190	271.078	183.357	72.720	I <--> II		
829.000	188.615	338.910	183.357	128.953	TRANSITION		
900	188.615	354.410	196.248	142.345	−279.582	−187.213	10.866
1000	188.615	374.282	213.076	161.206	−274.001	−177.251	9.259
1062.000	188.615	385.628	222.821	172.901	II <--> LIQUID		
1062.000	191.795	404.224	222.821	192.649	TRANSITION		
1100	191.795	410.966	229.205	199.937	−248.784	−168.546	8.004
1200	191.795	427.655	245.057	219.117	−243.368	−161.493	7.030
1300	191.795	443.006	259.702	238.296	−238.222	−154.880	6.223
1400	191.795	457.220	273.309	257.476	−233.365	−148.654	5.546
1500	191.795	470.452	286.016	276.655	−228.808	−142.764	4.971
1600	191.795	482.830	297.934	295.834	−224.564	−137.168	4.478
1700	191.795	494.458	309.156	315.014	−220.648	−131.827	4.051
1800	191.795	505.421	319.758	334.193	−268.516	−124.563	3.615
1900	191.795	515.790	329.805	353.373	−264.989	−116.662	3.207
2000	191.795	525.628	339.352	372.552	−261.486	−108.946	2.845
2100	191.795	534.986	348.447	391.732	−258.004	−101.404	2.522
2200	191.795	543.908	357.130	410.911	−254.543	−94.028	2.233
2300	191.795	552.434	365.438	430.091	−251.101	−86.809	1.972
2400	191.795	560.596	373.401	449.270	−247.677	−79.740	1.735
2500	191.795	568.426	381.046	468.450	−244.268	−72.812	1.521
2600	191.795	575.948	388.399	487.629	−240.874	−66.021	1.326
2700	191.795	583.187	395.480	506.809	−237.491	−59.360	1.148
2800	191.795	590.162	402.309	525.988	−234.121	−52.825	0.985
2900	191.795	596.892	408.903	545.167	−230.762	−46.409	0.836
3000	191.795	603.394	415.279	564.347	−227.413	−40.109	0.698
3100	191.795	609.683	421.449	583.526	−224.074	−33.921	0.572
3200	191.795	615.772	427.427	602.706	−1351.248	−12.274	0.200
3300	191.795	621.674	433.224	621.885	−1342.966	29.440	−0.466
3400	191.795	627.400	438.851	641.065	−1334.689	70.904	−1.089
3500	191.795	632.959	444.318	660.244	−1326.421	112.125	−1.673
3600	191.795	638.362	449.634	679.424	−1318.162	153.109	−2.222
3700	191.795	643.617	454.806	698.603	−1309.915	193.864	−2.737
3800	191.795	648.732	459.842	717.783	−1301.683	234.397	−3.222

PREVIOUS: CURRENT: December 1976

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = 186.48 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -301.11 \pm 25.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The only measured value of $\Delta_f H°(298.15\ K)$ for Ni_3S_4 is based on the emf data of DeRanter and Breckpot.[1] Our 3rd law analysis of their data yields $\Delta_f H°(298.15\ K) = -71.0\ kcal \cdot mol^{-1}$. A value of $-72.9\ kcal \cdot mol^{-1}$ can be estimated assuming the same contribution per gram atom in NiS and Ni_3S_2.[2] The adopted value, $\Delta_f H°(298.15\ K) = -72.0 \pm 6.0\ kcal \cdot mol^{-1}$, lies approximately midway between the above values and is chosen so that $\Delta_r G(629\ K) = 0$ for reaction $Ni_3S_4(cr) = 2\ NiS(cr) + NiS_2(cr)$.[2] This temperature represents the decomposition point of $Ni_3S_4(cr)$.[3,4]

Heat Capacity and Entropy

Since there are no measured values for the heat capacity of Ni_3S_4 it is estimated as follows. The value of $C_p°(298.15\ K)$ is estimated assuming the same contribution per gram atom as in NiS and Ni_3S_2,[2] yielding a value of $39.39\ cal \cdot K^{-1} \cdot mol^{-1}$. The value at the melting point is estimated assuming a contribution of $7.25\ cal \cdot K^{-1} \cdot g\text{-}atom^{-1}$ and the heat capacity is assumed to be linear between these two points.[5] This leads to $C_p°(cal \cdot K^{-1} \cdot mol^{-1}) = 29.153 \pm 0.03434\ T$.

The value of $S°(298.15\ K)$ is estimated assuming the same contribution per gram atom as in NiS and Ni_3S_2.[2] This estimate is subject to a rather large uncertainty since Ni_3S_4 has a spinel structure.[6] Navrotsky and Kleppa[7] showed that the entropies of oxide spinels vary by $\pm 3.7\ cal \cdot K^{-1} \cdot mol^{-1}$ depending on the distribution of cations among the available octahedral and tetrahedral sites.

Decomposition Data

The decomposition temperature of Ni_3S_4 is 629 ± 3 K.[3,4] It decomposes according to $Ni_3S_4(cr) = 2\ Ni_{1-x}S(cr) + NiS_2(cr)$. As mentioned above, $\Delta_f H°(298.15\ K)$ for $Ni_3S_4(cr)$ was chosen so that $\Delta_r G°(629\ K)$ for this reaction is zero. The value of $\Delta_r H°(629\ K)$ for this reaction, as calculated using auxiliary JANAF data,[2] is $2.2\ kcal \cdot mol^{-1}$. Kullerud and Yund[4] calculate $\Delta_r H°(629\ K) = +7.0\ kcal \cdot mol^{-1}$ for this reaction based on the volume change as calculated from cell dimensions for the three compounds.

Phase Data

The known crystal species in the Ni–S system include NiS, Ni_3S_2, Ni_3S_4, NiS_2, and Ni_7S_6.[3] The first four species occur naturally as minerals and we have prepared JANAF Thermochemical Tables for these species.[2] The species Ni_7S_6 (sometimes reported as Ni_9S_8 or Ni_6S_5) does not occur as a mineral and we have not prepared a table since there is a lack of thermochemical data. It is interesting to note that Ni_2S_3 does not occur as a stable species even though stable M_2S_3 species have been observed for Cr, Fe, and Co.[8] Estimates of $\Delta_f H°(298.15\ K)$ for Ni_2S_3 range from +225 to +484 $kcal \cdot mol^{-1}$.[9] Although Moody and Thomas[9] acknowledge large uncertainties in their calculations, they are unlikely to be in error to the extent necessary to predict stability for $Ni_2S_3(cr)$.

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[1] C. DeRanter and R. Breckpot, Bull. Soc. Chim. Belg. 78, 503 (1969).
[2] JANAF Thermochemical Tables: NiS(cr), Ni_3S_2(cr), 12–31–76; NiS_2(cr), 3–31–77.
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Nickel Sulfide (Ni_3S_4) Ni_3S_4(cr)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	164.808	186.481	186.481	0.	−301.115	−291.767	51.116
300	165.076	187.501	186.484	0.305	−301.122	−291.709	50.791
400	179.439	236.957	193.130	17.531	−310.469	−288.149	37.628
500	193.807	278.542	206.155	36.193	−316.421	−281.917	29.452
600	208.171	315.147	221.326	56.292	−320.495	−274.604	23.906
700	222.539	348.315	237.133	77.828	−322.315	−266.754	19.905
800	236.906	378.969	252.969	100.800	−321.447	−258.855	16.902
900	251.270	407.702	268.581	125.209	−531.454	−246.842	14.326
1000	265.638	434.919	283.865	151.054	−522.601	−215.682	11.266
1100	280.002	460.911	298.787	178.336	−512.576	−185.466	8.807

PREVIOUS: CURRENT: March 1977

Nickel Sulfide (Ni_3S_4) Ni_3S_4(cr)

Continued from page 1708

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[8]JANAF Thermochemical Tables: S_2(g), 12-31-65; H_2S(g), 12-31-65; NiS(cr), 12-31-76; Ni_3S(cr), 12-31-76.
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