Heat capacities of iron disulfides Thermodynamics of marcasite from 5 to 700 K, pyrite from 300 to 780 K, and the transformation of marcasite to pyrite[a]

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The heat capacity of purified natural marcasite has been determined by adiabatic-shield calorimetry in the region 5 to 700 K where it transforms to pyrite exothermically. Values of thermodynamic functions at 298.15 K are C_p, $\{S°(T) - S°(0)\}$, and $\{H°(T) - H°(0)\}$ are 14.92 cal$_{th}$ K^{-1} mol^{-1}, 12.88 cal$_{th}$ K^{-1} mol^{-1}, and 2328 cal$_{th}$ mol^{-1}, respectively, for marcasite (FeS$_2$). Our earlier measurements on pyrite have been extended to 770 K, and show that the heat capacity of marcasite is slightly higher than that of pyrite over the entire range of mutual existence. The transformation to pyrite is significantly exothermic at 700 K, $\Delta H_t = -(1.05 \pm 0.05)$ kcal$_{th}$ mol^{-1}, and correspondingly, $H°(T = 0$, marcasite) $- H°(T = 0$, pyrite) $= (0.99 \pm 0.05)$ kcal$_{th}$ mol^{-1}. Marcasite is thus metastable with regard to pyrite over the whole temperature region and owes its formation and persistence to kinetic factors. At 298.15 K the standard enthalpies, entropies, and Gibbs energies of formation for FeS$_2$ phases are:

	Pyrite	Marcasite
$\Delta H_f°$/kcal$_{th}$ mol^{-1}	-41.5 ± 0.5	-40.5 ± 0.5
$\Delta S_f°$/cal$_{th}$ K^{-1} mol^{-1}	$-9.0_7 \pm 0.1$	$-8.8_4 \pm 0.1$
$\Delta G°$/kcal$_{th}$ mol^{-1}	-38.8 ± 0.5	-37.9 ± 0.5

1. Introduction

Iron disulfide occurs in nature (and can be prepared in the laboratory also) in two polymorphic forms, marcasite and pyrite. While a considerable amount of thermo-dynamic data exists for pyrite,[1, 2] such data are virtually unknown for marcasite, except for some measurements of its enthalpy of combustion.[3–5] In order to remedy this situation and to evaluate the stability conditions for the polymorphs, the heat capacity of marcasite has been determined from 5 K to the temperature region where

it transforms to pyrite. Measurements on the previously studied pyrite sample[6] have been extended to 770 K.

Pyrite is formed under widely varying conditions, while the formation of marcasite is subject to strict limitations. Hydrothermal laboratory experiments have shown[7–10] that the formation of pyrite is favored at elevated temperatures in neutral or slightly basic solutions, while marcasite forms in colder, more acidic solutions. The results of Rickard[11] indicate that the formation of marcasite depends on the reaction between sulfur and a pre-existing iron sulfide, the tetragonal $Fe_{1+x}S$[12] (mackinawite)· Marcasite has so far not been prepared by dry methods, and this prompted Kullerud[13] to speculate that H–S bonds were of importance for its formation. Rickard[11] contends that water may be of importance in the formation of marcasite, but relates this to an enhanced formation reaction at temperatures where the marcasite-to-pyrite transformation is slow. In accordance with this, pyrite and marcasite are often found together both under laboratory conditions and in nature, as is commonly the case for monotropic polymorphic forms. It should also be noted that some natural crystals of the marcasite habit have, in fact, already undergone transformation to pyrite or do so on crushing.[14,15] While Wöhler[16] was not able to observe marcasite transforming to pyrite or *vice versa* at 720 K, and both Cavazzi[3] and Mixter[4] reported that the enthalpy of combustion of marcasite is equal to that of pyrite, Allen *et al.*[7] contended that marcasite transforms monotropically and exothermically to pyrite above 700 K. The inversion of marcasite has been studied by X-ray single crystal methods by Fleet.[17] Experience with several samples indicated that the transformation was partially complete after heating for 12 h at 700 K and essentially complete within less than 4 h at 750 K. The irreversibility of this transformation has been noted by many investigators, but quantitative information about the instability of marcasite from heat-capacity and enthalpy-of-transformation measurements is obviously needed. Furthermore, the possibility of a limited stability range of marcasite at lower temperature as a consequence of subtle differences in vibrational properties should not be overlooked, although it seems *a priori* more reasonable that the heat capacity of marcasite be higher than that of structurally related pyrite due to the larger molar volume of the former.

Finally, the question of compositional differences between pyrite and marcasite needs to be considered. After an evaluation of the available analytical data by Buerger[18] the composition $FeS_{1.985}$ was claimed for marcasite, while pyrite was judged to be stoichiometric. From decomposition-pressure measurements and magnetic results Juza and Biltz[19] concluded that pyrite had a range of homogeneity from FeS_2 to $FeS_{1.94}$. In the absence of further confirmation the latter conclusion seems doubtful. A slight compositional difference between marcasite and pyrite might, however, well be present but has not been conclusively established.[13,20]

2. Experimental

SAMPLE

The natural marcasite sample from near Carterville, Jasper County, Mo., consisted of crystal fragments of varying mass up to about 5 g. It was kindly supplied by Dr R. A. Robie of the U.S. Geological Survey.

Repeated chemical analyses of some crystal fragments by Laura Reichen gave (46.04 ± 0.1) mass per cent iron and (53.10 ± 0.1) mass per cent sulfur (theoretical 46.55 and 53.45 mass per cent, respectively). In addition, a trace of manganese and a small insoluble residue were noted. The iron to sulfur ratio is seen to be very closely stoichiometric (1/2.00). Semiquantitative spectrographic analyses by H. W. Worthing revealed mass percentages: Ag, 0.0007; Al, 0.005; Ba, 0.003; Ca, 0.0007; Cr, 0.00015; Cu, 0.015; Mn, 0.0001; Ni, 0.001; Pb, 0.2; Si, 0.01; Sn, 0.007. The following elements were not found: As, Au, B, Be, Bi, Cd, Ce, Co, Ga, Ge, Hf, Hg, In, K, La, Li, Mo, Na, Nb, P, Pd, Pt, Re, Sb, Sc, Ta, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr. Thus, the only significant concentration of trace metal detected was that of lead, probably present in the form of galena.

X-ray photographs and polished sections of different crystals used in the determinations showed the presence of the orthorhombic marcasite phase as the major component. The lattice constants, determined in an 11.46 cm diameter Straumanis-type camera with iron radiation $[\lambda(FeK\alpha_1) = 193.597$ pm] are: $a = (444.4 \pm 0.1)$, $b = (542.5 \pm 0.1)$, $c = (338.6 \pm 0.1)$ pm. They compare well with the recent results by Brostigen and Kjekshus:[21] $a = (444.31 \pm 0.09)$, $b = (542.45 \pm 0.09)$, $c = (338.71 \pm 0.06)$ pm]. In addition, smaller amounts of pyrite were present. An estimate of the average amount was obtained by comparing X-ray powder photographs of small fragments from about 10 per cent of the crystals with those of prepared mixtures containing 5 and 10 per cent pyrite. The amount of pyrite in the sample was found on this basis to be (6.5 ± 2.5) per cent.

After heating to 770 K in the calorimeter, only pyrite-lines were found on the powder photographs and the lattice constant of the sample was $a = (540.6 \pm 0.1)$ pm.

The pyrite sample was the same as used in the low-temperature heat-capacity study by Grønvold and Westrum.[6] It was from the Bosmo Mine, Nordland, Norway.

CALORIMETRIC TECHNIQUE

5 to 350 K, University of Michigan. The Mark II cryostat and adiabatic method employed have been described.[22] A gold-plated copper calorimeter (W-17) with a volume of 93 cm³ was used. Helium gas was added (76 Torr at 300 K) to improve thermal equilibration.† The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type platinum resistance thermometer (A-3) located in a central well in the calorimeter.

300 to 700 K, University of Oslo. The calorimetric apparatus and measuring technique have been described.[23] The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed quartz tube of about 50 cm³ volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

Calibrations and adjustments. The platinum resistance thermometer for the low-temperature calorimeter had been calibrated by the U.S. National Bureau of Stan-

† Throughout this paper Torr = (101.325/760) kPa; atm = 101.325 kPa; cal$_{th}$ = 4.184 J.

dards, and that for the high-temperature calorimeter locally, at the ice, steam, and zinc points. Temperatures are judged to correspond to IPTS-68 within 0.02 K from 4 to 300 K, and within 0.05 K above this temperature. Energy inputs were measured with reference to instruments calibrated by the U.S. National Bureau of Standards.

The heat capacities of the empty calorimeters were determined in separate series of experiments. It represented from 45 to 80 per cent of the total for the low-temperature calorimeter, and about 54 per cent for marcasite and 50 per cent for pyrite for the high-temperature calorimeter.

Small corrections were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in amounts of indium+tin solder, helium gas, and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the quartz containers for the high-temperature calorimeter. The mass of marcasite sample used was 130.833 g in the low-temperature calorimeter and 117.184 g in the high-temperature calorimeter, and the mass of pyrite used in the high-temperature calorimeter was 139.974 g.

3. Results and discussion

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES

The measured molar heat capacities for FeS_2 (marcasite) in the region 5 to 700 K and for pyrite in the region 330 to 770 K are presented in table 1. The temperature increments of the measurements can usually be deduced from the adjacent mean temperatures. When necessary, corrections have been applied for the finite temperature increments to obtain the limiting values of $\Delta H/\Delta T$. The measurements are considered to have a standard deviation of about 5 per cent at 5 K, 1 per cent at 10 K, and less than 0.1 per cent in the region 25 to 350 K for the low-temperature calorimeter and 0.3 per cent for the high-temperature calorimeter.

The heat capacity of marcasite is slightly higher than that of pyrite over its entire range of existence. This is shown as a difference plot in figure 1 over the region 5 to 350 K. The experimental heat capacities at higher temperatures are shown in figure 2.

Values of the heat capacity C_p, entropy $\{S°(T) - S°(0)\}$, enthalpy $\{H°(T) - H°(0)\}$, and function $-\{G°(T) - H°(0)\}/T$ are given for selected temperatures in table 2. They were obtained by appropriate computer evaluation of polynomials representing the heat capacity and extrapolation below 5 K for marcasite. Above 100 K the low-temperature heat capacity is characterized by a precision of ± 0.2 per cent, and the thermodynamic functions of ± 0.15 per cent equal to twice the standard deviation. In the higher temperature region, the corresponding precision indices are 0.4 and 0.2, respectively.

Coughlin[24] measured the enthalpy of pyrite from 298 to 980 K. The tabulated enthalpy increments are 4.2 per cent higher than the present at 400 K, 1.8 per cent higher at 500 K, 0.4 per cent higher at 600 K, and 0.3 per cent lower at 700 K. For marcasite only a mean heat capacity from drop-calorimetric experiments from 373 K to room temperature has been reported by Neumann[25] (15.98 cal_{th} K^{-1} mol^{-1}).

TABLE 1. Heat capacities of marcasite and pyrite

$[M(FeS_2) = 119.98 \text{ g mol}^{-1}; \text{cal}_{th} = 4.184 \text{ J}]$

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
		FeS₂, Marcasite (University of Michigan)					

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
	Series I	7.64	0.0038	49.63	0.7331		Series V
121.38	6.548	8.56	0.0049	54.10	0.9500	227.58	12.951
130.28	7.312	9.52	0.0070	59.20	1.243	235.94	13.251
137.84	7.931	10.54	0.0096	64.46	1.591	244.64	13.544
145.18	8.499	11.65	0.0106	69.95	1.984	253.54	13.814
152.37	9.028	12.88	0.0146	75.67	2.430	262.42	14.046
159.51	9.519	14.26	0.0190	80.72	2.866	271.02	14.282
167.06	10.010	15.79	0.0242	89.92	3.423	280.04	14.506
173.47	10.409	17.51	0.0320	93.18	3.985	289.13	14.721
182.79	10.939	19.43	0.0429	99.77	4.582	298.20	14.914
191.63	11.398	21.56	0.0575	106.78	5.228	305.47	15.05
200.14	11.793	23.79	0.0771	114.32	5.915	315.37	15.27
208.41	12.180	26.14	0.1021	122.49	6.640	325.01	15.44
216.44	12.518	28.78	0.1353			334.42	15.60
224.48	12.832	31.68	0.1773		Series III	341.90	15.71
		34.20	0.2260		ΔH detn A	347.52	15.79
	Series II	37.87	0.3127				
6.06	0.0025	41.88	0.4301		Series IV		
7.02	0.0027	45.81	0.5708		ΔH detn B		

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
	FeS₂, Marcasite (University of Oslo)						
	Series I	429.43	16.79	557.77	17.57	651.67	18.12
314.46	15.25	440.79	16.90	570.08	17.63	663.73	18.20
326.20	15.44	452.27	16.99	582.29	17.76	675.80	18.24
337.97	15.62	463.85	17.07	594.48	17.79	687.92	18.34
349.72	15.79	475.45	17.16	606.45	17.87	700.19	17.78
361.08	16.07	487.07	17.26	618.48	17.90		ΔH detn
372.72	16.22	498.74	17.33	630.56	17.93	736.32	18.34
384.08	16.38	510.44	17.44	642.68	18.05	748.73	18.50
395.42	16.45	522.14	17.47			761.09	18.49
406.76	16.65	533.86	17.52		Series II	773.44	18.58
418.09	16.72	545.70	17.55	639.61	18.00		

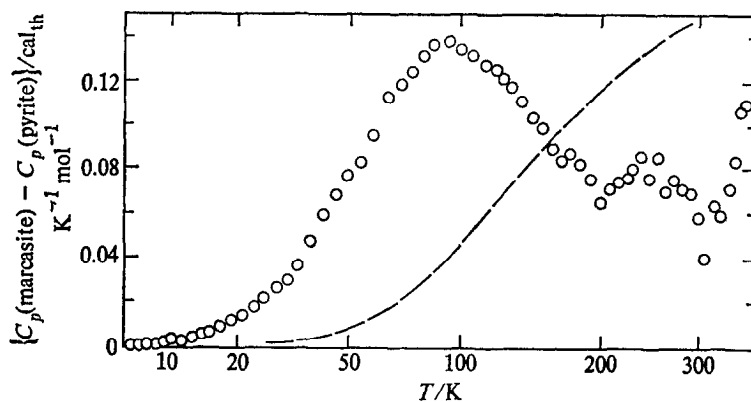| $\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
	FeS₂, Pyrite (University of Oslo)						
	Series I	464.47	17.03	604.70	17.77	749.80	18.40
337.88	15.56	475.09	17.03	615.67	17.82	761.71	18.44
348.55	15.74	485.76	17.12	626.68	17.85	773.56	18.51
359.18	15.92	496.47	17.20	637.73	17.92		
369.77	16.07	507.22	17.23	648.82	17.95		Series II
380.32	16.21	517.97	17.30	659.94	18.01	300.38	14.93
390.84	16.34	528.73	17.38	671.08	18.14	311.19	15.19
401.35	16.47	539.50	17.45	682.25	18.20	321.94	15.32
411.84	16.61	550.30	17.51	693.46	18.18	332.64	15.53
422.33	16.70	561.11	17.53	704.73	18.21	343.30	15.69
432.82	16.82	571.96	17.63	716.04	18.32		
443.33	16.91	582.84	17.70	727.37	18.38		
453.88	16.96	593.75	17.76	738.18	18.37		

FIGURE 1. Deviation of the low-temperature heat capacity of marcasite (○) from the smoothed values for pyrite. The dashed line indicates 0.1 per cent deviation.
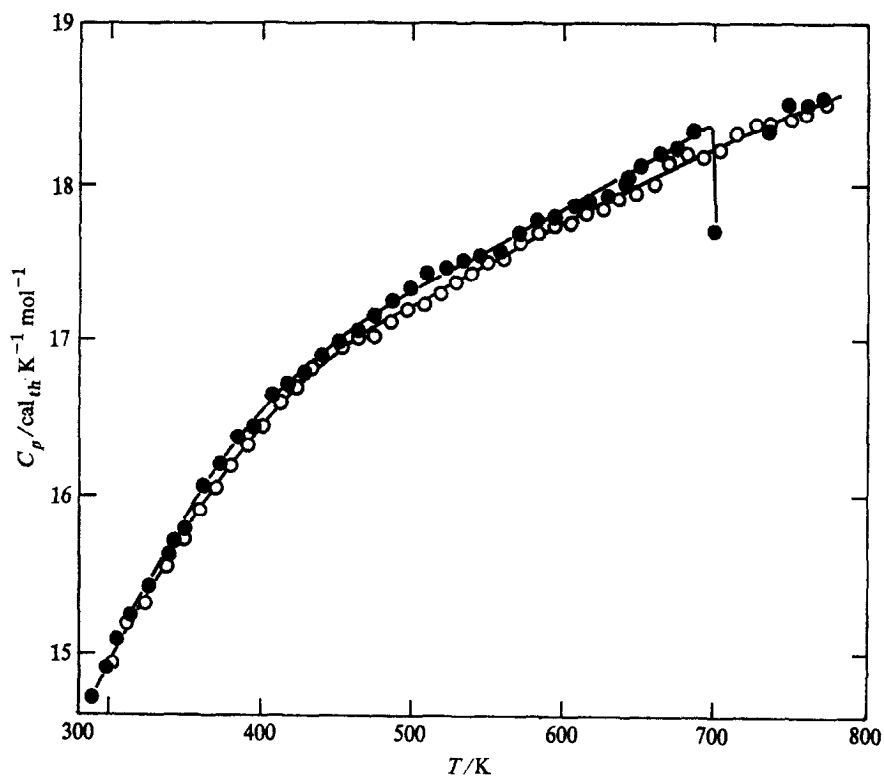

FIGURE 2. Heat capacities of marcasite (●) and pyrite (○) at higher temperatures.

TABLE 2. Thermodynamic properties of marcasite and pyrite
$(\text{cal}_{th} = 4.184 \text{ J})$

$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\, K^{-1}\, mol^{-1}}$	$\dfrac{\{S°(T) - S°(0)\}}{\text{cal}_{th}\, K^{-1}\, mol^{-1}}$	$\dfrac{\{H°(T) - H°(0)\}}{\text{cal}_{th}\, mol^{-1}}$	$\dfrac{-\{G°(T) - H°(0)\}/T}{\text{cal}_{th}\, K^{-1}\, mol^{-1}}$
		Marcasite		
5	(0.0016)	(0.0005)	(0.002)	(0.0001)
10	0.0072	0.0030	0.022	0.0009
15	0.0213	0.0083	0.089	0.0024
20	0.0470	0.0176	0.254	0.0049
25	0.0885	0.0322	0.585	0.0088
30	0.1517	0.0536	1.175	0.0144
35	0.2438	0.0834	2.150	0.0220
40	0.3714	0.1239	3.672	0.0321
45	0.5391	0.1769	5.931	0.0451
50	0.7492	0.2442	9.134	0.0615
60	1.294	0.4265	19.21	0.1063
70	1.988	0.6764	35.51	0.1690
80	2.805	0.9940	59.39	0.2516
90	3.696	1.376	91.87	0.3547
100	4.612	1.812	133.4	0.4782
110	5.529	2.295	184.1	0.6211
120	6.424	2.815	243.9	0.7820
130	7.282	3.363	312.5	0.9593
140	8.093	3.933	389.4	1.151
150	8.851	4.517	474.1	1.356
160	9.552	5.111	566.2	1.572
170	10.20	5.710	665.0	1.798
180	10.78	6.309	824.6	2.152
190	11.32	6.907	880.6	2.273
200	11.81	7.501	996.3	2.519
210	12.26	8.088	1116.7	2.771
220	12.67	8.668	1241.3	3.026
230	13.04	9.239	1369.9	3.283
240	13.38	9.801	1502.0	3.543
250	13.69	10.354	1637.4	3.805
260	13.99	10.897	1775.8	4.067
270	14.26	11.430	1917.2	4.330
273.15	14.34	11.60	1962	4.413
280	14.51	11.953	2060.9	4.593
290	14.74	12.466	2207.2	4.855
298.15	14.92	12.88	2328	5.069
300	14.96	12.970	2355.7	5.118
350	15.83	15.346	3126.8	6.412
400	16.52	17.512	3937.4	7.668
450	16.99	19.487	4775.9	8.874
500	17.33	21.296	5634.5	10.027
550	17.58	22.959	6507.4	11.128
600	17.81	24.499	7392.1	12.179
650	18.09	25.935	8289.2	13.182
700	18.40	27.287	9201.6	14.142

TABLE 2—continued

$\frac{T}{K}$	$\frac{C_p}{cal_{th} \ K^{-1} \ mol^{-1}}$	$\frac{\{S°(T) - S°(0)\}}{cal_{th} \ K^{-1} \ mol^{-1}}$	$\frac{\{H°(T) - H°(0)\}}{cal_{th} \ mol^{-1}}$	$\frac{-\{G°(T) - H°(0)\}/T}{cal_{th} \ K^{-1} \ mol^{-1}}$
		Pyrite		
10	0.0056	0.0018	0.0139	0.0004
25	0.0735	0.0239	0.4406	0.0062
50	0.6705	0.2057	7.820	0.0493
100	4.471	1.693	126.1	0.4324
200	11.72	7.300	977.3	2.413
273.15	14.28	11.37	1937	4.277
298.15	14.86	12.65	2302	4.926
300	14.90	12.740	2329.7	4.974
350	15.66	15.111	3097.3	6.255
400	16.45	17.264	2905.2	7.501
450	16.91	19.230	4740.1	8.697
500	17.24	21.030	5594.2	9.842
550	17.49	22.685	6462.6	10.935
600	17.74	24.218	7343.4	11.979
650	18.00	25.648	8236.7	12.976
700	18.24	26.990	9142.7	13.929
750	18.42	28.255	10059.3	14.843
780	18.51	28.979	10613.2	15.373

THE MARCASITE-TO-PYRITE TRANSFORMATION

The higher-temperature heat-capacity measurements on marcasite were quite normal until the sixth energy input of Series II produced a somewhat higher temperature increment and brought the temperature up to 706.43 K. Here the drift-rate gradually changed from a slightly negative value of about -0.0009 K min^{-1} to large positive values after a period of 2 h. The subsequent gradual temperature increase was followed for a further 96 h, figure 3, at which time the temperature was estimated to be not more than (0.15 ± 0.25) K from the limiting value, T_∞. The enthalpy of transformation (including -8.3 cal$_{th}$ mol^{-1} from Series II, run 6) was (-979 ± 25) cal$_{th}$ mol^{-1} for the sample which contained (6.5 ± 2.5) per cent of pyrite. Hence, the enthalpy of transformation of marcasite to pyrite at 700 K is $\Delta H_t = (-1050 \pm 50)$ cal$_{th}$ mol^{-1}.

When the heat-capacity measurements were continued after 96 h a slight positive drift was noted due to the transformation of the remaining amount of marcasite, but this decay was not studied further. The heat capacity corresponded closely to that of pyrite, and X-ray powder photographs taken of the sample after completion of the measurements showed the presence of pyrite only.

The heat capacity of the pyrite sample increased gradually over the temperature range 350 to 770 K without any sign of transformation. The values were 0.5 to 1.0 per cent lower than for marcasite at the corresponding temperature. They joined very well with the low-temperature measurements. In the absence of a zero-point entropy in this system, marcasite even in the vicinity of the transformation temperature is
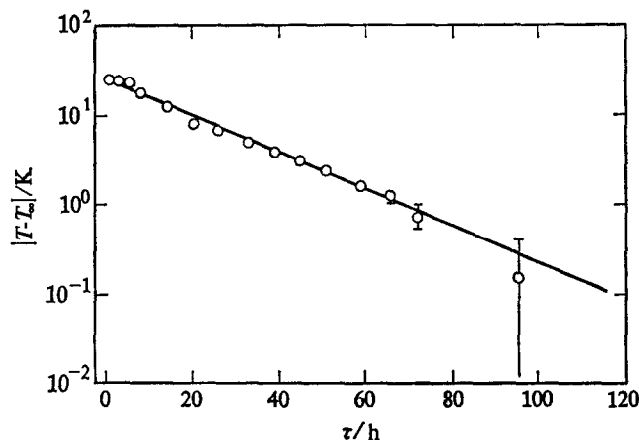
FIGURE 3. Equilibration times τ for the marcasite-to-pyrite transformation.

thermodynamically metastable with respect to pyrite; hence the transformation is monotropic and irreversible. Consequently, we cannot ascribe an entropy increment to the transformation and instead utilize an enthalpy cycle for the marcasite-pyrite system through $T = 0$. Taking into account the enthalpy increment for the marcasite to pyrite transformation at 700 K, the $\{H°(T = 0, \text{marcasite}) - H°(T = 0, \text{pyrite})\}$ is found to be (0.99 ± 0.05) kcal$_{th}$ mol^{-1}. This value should, therefore be incorporated into $\{G°(T) - H°(0)\}/T$ for marcasite for chemical thermodynamic calculations. Moreover, marcasite is seen to be clearly metastable with respect to pyrite above $T = 0$. For example, at 298.15 K the value of $\Delta G°(\text{marcasite} \rightarrow \text{pyrite})$ is (-0.95 ± 0.05) kcal$_{th}$ mol^{-1}.

Our results together with the critically evaluated values of $\Delta H_f°(\text{pyrite})$ from Mills's[1] and from Robie and Waldbaum's[2] reviews together with entropies for iron[26] and sulfur[26] yield the following standard enthalpies, entropies, and Gibbs energies of formation for FeS$_2$ at 298.15 K:

	Pyrite	Marcasite
$\Delta H_f°/\text{kcal}_{th}\,\text{mol}^{-1}$	-41.5 ± 0.5	-40.5 ± 0.5
$\Delta S_f°/\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}$	$-9.0_7 \pm 0.1$	$-8.8_4 \pm 0.1$
$\Delta G_f°/\text{kcal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}$	-38.8 ± 0.5	-37.9 ± 0.5

Hence, the geological occurrence of pyrite pseudomorphs after marcasite is consistent with above interpretation, since marcasite presumably occurs in low-temperature hydrothermal deposits and apparently occasionally transforms at temperatures well below 700 K to pyrite.

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