

Copper (Cu)

 $A_1 = 63.546$ Copper (Cu)

REFERENCE STATE

0 to 1358 K crystal
1358 to 2843.261 K liquid
above 2843.261 K ideal monatomic gas

Refer to the individual tables for details.

Cu₁(ref)

T/K	C _p	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
		$S^\circ - [G^\circ - H^\circ(T_r)]/T$ J·K ⁻¹ ·mol ⁻¹	$H^\circ - H^\circ(T_r)$ kJ·mol ⁻¹	$\Delta_f H^\circ$ kJ·mol ⁻¹	ΔG° kJ·mol ⁻¹	
0	0	0	INFINITE	-5.007	0	0
100	16.010	10.034	53.114	-4.338	0	0
200	22.631	23.730	33.334	-2.325	0	0
298.15	24.442	33.164	0	0	0	0
300	24.462	33.315	33.164	0.045	0	0
400	25.318	40.484	34.136	2.539	0	0
500	25.912	46.206	35.997	5.105	0	0
600	26.481	50.982	38.107	7.725	0	0
700	26.996	55.103	40.247	10.389	0	0
800	27.494	58.739	42.336	13.123	0	0
900	28.049	62.009	44.343	15.899	0	0
1000	28.662	64.994	46.261	18.733	0	0
1100	29.479	67.763	48.091	21.638	0	0
1200	30.519	70.368	49.840	24.633	0	0
1300	32.143	72.871	51.516	27.762	0	0
1358.000	33.353	74.300	52.459	29.660	0	0
1358.000	32.844	83.974	52.459	42.798	0	0
1400	32.844	84.974	53.419	44.177	0	0
1500	32.844	87.240	55.599	47.462	0	0
1600	32.844	89.360	57.644	50.746	0	0
1700	32.844	91.351	59.569	54.031	0	0
1800	32.844	93.229	61.387	57.315	0	0
1900	32.844	95.004	63.110	60.600	0	0
2000	32.844	96.689	64.747	63.884	0	0
2100	32.844	98.292	66.307	67.168	0	0
2200	32.844	99.819	67.795	70.453	0	0
2300	32.844	101.279	69.220	73.737	0	0
2400	32.844	102.677	70.585	77.022	0	0
2500	32.844	104.018	71.896	80.306	0	0
2600	32.844	105.306	73.156	83.591	0	0
2700	32.844	106.546	74.370	86.875	0	0
2800	32.844	107.740	75.540	90.159	0	0
2843.261	32.844	108.244	76.034	91.580	0	0
2843.261	24.379	213.995	76.034	392.257	0	0
3000	24.653	214.479	78.738	393.648	0	0
3000	25.147	215.323	83.277	396.138	0	0
3100	25.652	216.156	87.550	398.678	0	0
3200	26.162	216.978	91.582	401.268	0	0
3300	26.673	217.791	95.394	403.910	0	0
3400	27.180	218.595	99.006	406.603	0	0
3500	27.680	219.390	102.434	409.346	0	0
3600	28.168	220.177	105.694	412.138	0	0
3700	28.641	220.955	108.759	414.979	0	0
3800	29.097	221.723	111.780	417.868	0	0
3900	29.533	222.486	114.759	420.798	0	0
4000	29.948	223.239	117.696	423.772	0	0
4100	30.339	223.984	119.889	426.786	0	0
4200	30.707	224.719	122.377	429.839	0	0
4300	31.051	225.446	124.765	432.927	0	0
4400	31.379	226.163	127.062	436.048	0	0
4500	31.693	226.872	129.272	439.200	0	0
4600	31.936	227.571	131.401	442.380	0	0
4700	32.185	228.260	133.455	445.587	0	0
4800	32.413	228.940	135.437	448.817	0	0
4900	32.621	229.611	137.352	452.069	0	0
5000	32.809	230.272	139.204	455.340	0	0
5100	32.981	230.923	140.996	458.630	0	0
5200	33.137	231.565	142.731	461.936	0	0
5300	33.279	232.198	144.413	465.257	0	0
5400	33.409	232.821	146.045	468.591	0	0
5500	33.530	233.435	147.628	471.938	0	0
5600	33.641	234.040	149.166	475.297	0	0
5700	33.746	234.637	150.660	478.666	0	0
5800	33.845	235.224	152.113	482.046	0	0
5900	33.941	235.804	153.527	485.435	0	0
6000	34.035	236.375	154.903	488.834	0	0

PREVIOUS: June 1977 (1 atm)

CURRENT: June 1977 (1 bar)

Copper (Cu)

Cu₁(ref)

Copper (Cu)

CRYSTAL

Copper (Cu)

Cu₁(cr)

$$\Delta_f H^\circ(0 \text{ K}) = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = 0 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{sub}} H^\circ = 13.138 \pm 0.4 \text{ kJ mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = 33.164 \pm 0.04 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_{\text{m}} = 1358.0 \pm 0.2 \text{ K}$$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity and entropy of copper have been well established by the critical review of Furukawa *et al.*¹ Their recommended smoothed values are adopted with minor corrections for a change in the relative atomic mass from 63.54 to 63.546² and for a change to the International Practical Temperature Scale of 1968.³ These corrections increase the entropy at 298.15 K from 7.926 to 7.926 cal K⁻¹ mol⁻¹ and the enthalpy difference, $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$, from 1.1962 to 1.1967 kcal mol⁻¹. The values recommended by CODATA⁴ are those of Furukawa *et al.*¹

From 300 K to the melting point, the heat capacity selected by Hultgren *et al.*⁵ has been adopted, with correction for relative atomic mass and temperature scale, and has been joined smoothly with the adopted low temperature data. The measurements of Chekhovskoi and Gerasina,⁶ as given by their equation (300–900 K), are in excellent agreement with the selection of Hultgren *et al.*⁵ Also, while the data given by Brooks *et al.*⁷ (313–1193 K) were 1–2% higher than Hultgren's selected values, the later measurements of Yeh and Brooks⁸ on the same sample did not totally confirm the earlier results and measurements on a larger sample (370–870 K) are in good agreement with Hultgren *et al.*⁵ The same evaluation used by Hultgren *et al.*⁵ was used by two other tabulations^{9,10}, although there are small differences in the tabulated values.

Fusion Data

Righini *et al.*¹¹ reviewed the precise measurements of the freezing point of high-purity copper made since 1960. The mean value of five investigations is 1357.99 ± 0.24 (IPTS-68). Ergardt¹² found 1358.41 K and Righini *et al.*¹¹ measured $1357.98 \pm 0.1 \text{ K}$. We adopt $1358.0 \pm 0.2 \text{ K}$ for the melting point. As a secondary fixed point IPTS-68 uses 1357.6 K .¹³ The adopted value for $\Delta_{\text{fus}} H^\circ$ is based upon five measured values and an evaluation of $H^\circ(1358 \text{ K}) - H^\circ(298.15 \text{ K})$ for the solid and the liquid.

Source	$\Delta_{\text{fus}} H^\circ$, kcal mol ⁻¹
14	3.239
15	3.030
16	3.080
17	3.290 ± 0.275
18	3.107 ± 0.048

The average is $3.149 \text{ kcal mol}^{-1}$. Our least squares linear fit of the liquid enthalpy data of Wust, Meuthen, and Durrer¹⁴ leads to $\Delta_{\text{fus}} H^\circ = 3.139 \text{ kcal mol}^{-1}$, and with this change, the average of the five measured values is $3.129 \text{ kcal mol}^{-1}$.

We adopt $\Delta_{\text{fus}} H^\circ = 3.140 \pm 0.1 \text{ kcal mol}^{-1}$.

Sublimation Data

Refer to the ideal gas Cu(g) table for details.

References

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T/K	C _p ^a	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa		log K _r
		S°	-(G° - H°(T _r))/T	H° - H°(T _r)	ΔG°	
0	0	0	INFINITE	-5.007	0	0
100	16.010	10.034	33.414	-4.338	0	0
200	22.631	23.730	33.354	-2.325	0	0
250	23.782	28.915	33.563	-1.162	0	0
298.15	24.442	33.164	33.164	0	0	0
300	24.462	33.315	33.164	0.045	0	0
350	24.975	37.127	33.464	1.282	0	0
400	25.318	40.484	34.136	2.539	0	0
450	25.686	43.489	35.011	3.815	0	0
500	25.912	46.206	35.997	5.105	0	0
600	26.481	50.982	38.107	7.725	0	0
700	26.996	55.103	40.247	10.399	0	0
800	27.494	58.739	42.336	13.123	0	0
900	28.049	62.009	44.343	15.899	0	0
1000	28.662	64.994	46.261	18.733	0	0
1100	29.479	67.763	48.091	21.638	0	0
1200	30.519	70.368	49.840	24.633	0	0
1300	31.143	72.871	51.516	27.762	0	0
1358.000	31.353	74.300	52.459	29.660	CRYSTAL < - - -> LIQUID	- - -
1400	34.258	75.350	53.129	31.081	-13.097	0.406
1500	36.425	77.767	54.691	34.615	-12.847	1.363
1600	38.593	80.187	56.209	38.366	-12.381	2.296
1700	40.760	82.592	57.690	42.333	-11.697	-0.075
1800	42.928	84.983	59.140	46.518	-10.797	3.194
1900	45.095	87.362	60.563	50.919	-9.681	4.045
2000	47.263	89.730	61.962	55.537	-8.347	4.840
						-0.133
						-0.145

PREVIOUS December 1965

CURRENT: June 1971

Copper (Cu)

Cu₁(cr)

Copper (Cu) Cu₂(l)

$A_f = 63.546$ Copper (Cu)

$\Delta_f H^\circ(298.15 \text{ K}) = [11.857] \text{ kJ}\cdot\text{mol}^{-1}$
 $\Delta_{\text{liq}} H^\circ = 13.138 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$

Enthalpy of Formation
 The enthalpy of formation at 298.15 is calculated from that of the crystal by adding $\Delta_{\text{liq}} H^\circ$ and the difference in enthalpy, $H^\circ(1358 \text{ K}) - H^\circ(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy
 Since the critical evaluation of Hultgren *et al.*¹ and the selection of $7.80 \text{ cal K}^{-1}\cdot\text{mol}^{-1}$ for the heat capacity of liquid copper, there have been two experimental investigations. Chaudhuri *et al.*² measured enthalpies (1386–1887 K) by levitation heating aluminum block drop calorimetry and determined $C_p(l) = 7.89 \pm 0.41 \text{ cal K}^{-1}\cdot\text{mol}^{-1}$. Stephens³ found $C_p(l) = 8 \text{ cal K}^{-1}\cdot\text{mol}^{-1}$ by levitation heating liquid argon calorimetry (1428–2007 K). The scatter in the new liquid argon calorimetry data is large and is considered only in that it tends to support a "chronological increase" in $C_p(l)$ of copper. The enthalpy differences, $H^\circ(1358 \text{ K}) - H^\circ(298.15 \text{ K})$, derived from the measurements of Vollmer and Kohlhaus⁴ and Chaudhuri *et al.*² are in good agreement at about $10.228 \text{ kcal}\cdot\text{mol}^{-1}$ which we adopt. The scatter of liquid enthalpy measurements easily accommodates a wide range of values for $C_p(l)$; we adopt $7.85 \text{ cal K}^{-1}\cdot\text{mol}^{-1}$, an average of the value selected by Hultgren *et al.*¹ and the later measurement of Chaudhuri *et al.*² This value is assumed constant from 900 to 4000 K. A glass transition is assumed at 900 K below which the heat capacity is that of the crystal.

The entropy is calculated in a manner similar to that used to calculate the enthalpy of formation.

Fusion Data
 Refer to the crystal table for details.

Vaporization Data
 T_{vap} is the calculated temperature at which the Gibbs energy difference is zero for the reaction $\text{Cu}(l) = \text{Cu}(g)$. $\Delta_{\text{vap}} H^\circ$ is the difference in $\Delta_f H^\circ$ between gas and liquid at T_{vap} .

References
¹R. Hultgren, P. D. Desai, *et al.*, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio, 1973, copper evaluation dated (1969).
²A. K. Chaudhuri, D. W. Bonnelli, L. A. Ford, and J. L. Margrave, High Temp. Sci. 2, 203 (1970).
³H. P. Stephens, High Temp. Sci. 6, 156 (1974).
⁴O. Vollmer and R. Kohlhaus, Z. Metallk. 59, 273 (1968).

T/K	C_p°	S°	$-[G^\circ - H^\circ(T)]/T$	$H^\circ - H^\circ(T)$	$\Delta_f H^\circ$	ΔG°	log K _f
298.15	24.442	41.620	41.620	0.	11.857	9.336	-1.636
300	24.460	41.772	41.621	0.045	11.857	9.320	-1.623
350	24.973	45.583	41.921	1.282	11.857	8.898	-1.328
400	25.316	48.939	42.592	2.339	11.857	8.475	-1.107
450	25.484	51.944	43.467	3.614	11.857	8.052	-0.935
500	25.910	54.661	44.433	5.104	11.857	7.629	-0.797
600	26.478	59.436	46.563	7.724	11.857	6.784	-0.591
700	26.993	63.557	48.703	10.398	11.856	5.938	-0.443
800	27.491	67.193	50.791	13.121	11.856	5.093	-0.333
900	28.047	70.463	52.798	15.898	11.856	4.248	-0.247
900.000	28.047	70.463	52.798	15.898	GLASS <--> LIQUID TRANSITION		
1000	32.844	73.923	54.741	19.182	12.306	3.378	-0.176
1100	32.844	77.053	56.629	22.467	12.686	2.466	-0.117
1200	32.844	79.911	58.452	25.751	12.975	1.523	-0.066
1300	32.844	82.540	60.205	29.036	13.131	0.561	-0.023
1358.000	32.844	83.974	61.190	30.941	CRYSTAL <--> LIQUID		
1400	32.844	84.974	61.889	32.320	0.	0.	0.
1500	32.844	87.240	63.504	35.604	0.	0.	0.
1600	32.844	89.360	65.055	38.889	0.	0.	0.
1700	32.844	91.351	66.543	42.173	0.	0.	0.
1800	32.844	93.229	67.974	45.458	0.	0.	0.
1900	32.844	95.004	69.351	48.742	0.	0.	0.
2000	32.844	96.689	70.676	52.027	0.	0.	0.
2100	32.844	98.292	71.953	55.311	0.	0.	0.
2200	32.844	99.819	73.185	58.596	0.	0.	0.
2300	32.844	101.279	74.375	61.880	0.	0.	0.
2400	32.844	102.677	75.525	65.164	0.	0.	0.
2500	32.844	104.018	76.639	68.449	0.	0.	0.
2600	32.844	105.306	77.717	71.733	0.	0.	0.
2700	32.844	106.546	78.761	75.018	0.	0.	0.
2800	32.844	107.740	79.775	78.302	0.	0.	0.
2843.261	32.844	108.244	80.205	79.723	----	FUGACITY = 1 bar	----
2900	32.844	108.893	80.760	81.587	-300.204	5.996	-0.108
3000	32.844	110.006	81.716	84.871	-299.409	16.541	-0.288
3100	32.844	111.083	82.646	88.155	-298.665	27.060	-0.456
3200	32.844	112.126	83.531	91.440	-297.971	37.536	-0.615
3300	32.844	113.137	84.424	94.724	-297.328	48.031	-0.760
3400	32.844	114.117	85.291	98.009	-296.737	58.488	-0.899
3500	32.844	115.069	86.128	101.293	-296.195	68.927	-1.029
3600	32.844	115.995	86.945	104.578	-295.703	79.352	-1.151
3700	32.844	116.894	87.743	107.862	-295.259	89.764	-1.267
3800	32.844	117.770	88.521	111.147	-294.862	100.165	-1.377
3900	32.844	118.624	89.284	114.431	-294.509	110.556	-1.481
4000	32.844	119.455	90.026	117.715	-294.199	120.938	-1.579

PREVIOUS: December 1966

CURRENT: June 1977

Copper (Cu)

Cu₂(l)

Cu₁(cr,l)

A₁ = 63.546 Copper (Cu)

CRYSTAL-LIQUID

0 to 1358 K crystal
above 1358 K liquid
Refer to the individual tables for details.

Copper (Cu)

Enthalpy Reference Temperature = T _r = 298.15 K									
T/K	C _p ^a	J·K ⁻¹ ·mol ⁻¹		kJ·mol ⁻¹		H ^a - H ^a (T _r)	ΔG ^a	log K _f	
		S ^a	-(G ^a - H ^a (T _r))/T	S ^a	ΔH ^a				
0	0.	0.	INFINITE	0.	-5.007	0.	0.	0.	
100	16.010	10.034	53.414	0.	-4.338	0.	0.	0.	
200	22.631	23.730	35.354	0.	-2.325	0.	0.	0.	
250	23.782	28.915	33.563	0.	-1.162	0.	0.	0.	
298.15	24.442	33.164	33.164	0.	0.	0.	0.	0.	
300	24.462	33.315	33.164	0.	0.045	0.	0.	0.	
350	24.975	37.127	33.464	0.	1.282	0.	0.	0.	
400	25.318	40.484	34.136	0.	2.539	0.	0.	0.	
450	25.686	43.489	35.011	0.	3.815	0.	0.	0.	
500	25.912	46.206	35.997	0.	5.105	0.	0.	0.	
600	26.481	50.982	38.107	0.	7.725	0.	0.	0.	
700	26.996	55.103	40.247	0.	10.399	0.	0.	0.	
800	27.494	58.739	42.336	0.	13.123	0.	0.	0.	
900	28.049	62.009	44.343	0.	15.899	0.	0.	0.	
1000	28.662	64.994	46.261	0.	18.733	0.	0.	0.	
1100	29.479	67.763	48.091	0.	21.638	0.	0.	0.	
1200	30.519	70.368	49.840	0.	24.633	0.	0.	0.	
1300	32.143	72.871	51.516	0.	27.762	0.	0.	0.	
1358.000	33.353	74.300	52.459	0.	29.660	0.	0.	0.	
1358.000	32.844	83.974	52.459	0.	42.798	0.	0.	0.	CRYSTAL <- -> LIQUID TRANSITION
1400	32.844	84.974	53.419	0.	44.177	0.	0.	0.	
1500	32.844	87.240	55.599	0.	47.462	0.	0.	0.	
1600	32.844	89.360	57.644	0.	50.746	0.	0.	0.	
1700	32.844	91.351	59.569	0.	54.031	0.	0.	0.	
1800	32.844	93.229	61.387	0.	57.315	0.	0.	0.	
1900	32.844	95.004	63.110	0.	60.600	0.	0.	0.	
2000	32.844	96.689	64.747	0.	63.884	0.	0.	0.	
2100	32.844	98.292	66.307	0.	67.168	0.	0.	0.	
2200	32.844	99.819	67.795	0.	70.453	0.	0.	0.	
2300	32.844	101.279	69.220	0.	73.737	0.	0.	0.	
2400	32.844	102.677	70.585	0.	77.022	0.	0.	0.	
2500	32.844	104.018	71.896	0.	80.306	0.	0.	0.	
2600	32.844	105.306	73.156	0.	83.591	0.	0.	0.	
2700	32.844	106.546	74.370	0.	86.875	0.	0.	0.	
2800	32.844	107.740	75.540	0.	90.159	0.	0.	0.	
2843.261	32.844	108.244	76.034	0.	91.580	0.	0.	0.	
2900	32.844	108.893	76.671	0.	93.444	0.	0.	0.	
3000	32.844	110.006	77.764	0.	96.728	0.	0.	0.	
3100	32.844	111.083	78.821	0.	99.665	0.	0.	0.	
3200	32.844	112.126	79.846	0.	103.297	0.	0.	0.	
3300	32.844	113.137	80.839	0.	106.582	0.	0.	0.	
3400	32.844	114.117	81.804	0.	109.866	0.	0.	0.	
3500	32.844	115.069	82.741	0.	113.151	0.	0.	0.	
3600	32.844	115.995	83.652	0.	116.435	0.	0.	0.	
3700	32.844	116.894	84.538	0.	119.719	0.	0.	0.	
3800	32.844	117.770	85.401	0.	123.004	0.	0.	0.	
3900	32.844	118.624	86.242	0.	126.288	0.	0.	0.	
4000	32.844	119.455	87.062	0.	129.573	0.	0.	0.	
----- FUGACITY = 1 bar -----									
2900	32.844	108.893	76.671	0.	93.444	5.996	-0.108		
3000	32.844	110.006	77.764	0.	96.728	16.541	-0.288		
3100	32.844	111.083	78.821	0.	99.665	27.060	-0.456		
3200	32.844	112.126	79.846	0.	103.297	37.556	-0.613		
3300	32.844	113.137	80.839	0.	106.582	48.031	-0.760		
3400	32.844	114.117	81.804	0.	109.866	58.488	-0.899		
3500	32.844	115.069	82.741	0.	113.151	68.927	-1.029		
3600	32.844	115.995	83.652	0.	116.435	79.352	-1.151		
3700	32.844	116.894	84.538	0.	119.719	89.764	-1.267		
3800	32.844	117.770	85.401	0.	123.004	100.163	-1.377		
3900	32.844	118.624	86.242	0.	126.288	110.558	-1.481		
4000	32.844	119.455	87.062	0.	129.573	120.938	-1.579		

PREVIOUS.

CURRENT. June 1977

Copper (Cu)

Cu₁(cr,l)

Copper (Cu)

IDEAL GAS

A₁ = 63.546 Copper (Cu)Cu₁(g)

IP(Cu, g) = 62317.2 ± 0.5 cm⁻¹
 S°(298.15 K) = 166.397 ± 0.025 J K⁻¹ mol⁻¹

ΔH°(0 K) = 336.4 ± 1.2 kJ mol⁻¹
 ΔH°(298.15 K) = 337.6 ± 1.2 kJ mol⁻¹

Electronic Levels and Quantum Weights	g _e
State	cm ⁻¹
² S _{1/2}	0.000
² D _{3/2}	11202.565
² D _{5/2}	13245.432
² P _{1/2}	30535.302
² P _{3/2}	30783.683

Enthalpy of Formation

The adopted enthalpy of formation for Cu(g), ΔH°(298.15 K) = 337.6 ± 1.2 kJ mol⁻¹, is the value recommended by CODATA.¹ This value was based on the measurements of Edwards *et al.*,² Hersh, Morris and Zellars,³ Marshall *et al.*,⁴ McCormack *et al.*,⁵ Myles and Daltby,⁶ Grievson *et al.*,⁷ Kirschenbaum and Cahill,⁸ Krupkowski and Golonka⁹ and Ponslit and Bariaux.¹¹ Additional references are given in Hultgren *et al.*¹²

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,¹³ is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground state and the lowest lying levels, all levels listed by Moore,¹³ as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Cu(g), the thermodynamic functions are independent of the estimated missing levels (for n = 4–11), the cut off procedure, and the inclusion of n < 12 levels up to 6000 K; the Gibbs energy function showing variations of 0.001 J K⁻¹ mol⁻¹ at this temperature. The reported uncertainty in S°(298.15 K) is due to uncertainties in the relative atomic masses, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n > 11), and use of different fill and cut off procedures.¹⁴

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T/K	C _p J K ⁻¹ mol ⁻¹	S° - [G° - H°(T ₀)]/T J K ⁻¹ mol ⁻¹	H° - H°(T ₀) kJ mol ⁻¹	ΔG° kJ mol ⁻¹	log K _r
0	0	INFINITE	INFINITE	336.409	INFINITE
100	20.786	143.690	-6.197	337.819	-169.477
200	20.786	158.097	-4.119	338.454	-81.228
250	20.786	162.736	-2.040	337.883	-63.581
298.15	20.786	166.397	-1.001	337.761	-52.187
300	20.786	166.397	0	297.877	-51.822
350	20.786	166.525	0.038	297.630	-43.427
400	20.786	167.750	1.078	290.985	-37.135
450	20.786	174.953	2.117	284.369	-32.244
500	20.786	177.144	3.156	277.782	-28.334
600	20.786	180.933	4.196	271.222	-22.476
700	20.786	184.137	5.234	264.779	-18.299
800	20.786	186.913	6.274	258.450	-14.742
900	20.786	189.351	7.313	252.230	-11.741
1000	20.787	191.551	8.353	246.119	-9.226
1100	20.788	193.533	9.393	240.124	-7.111
1200	20.793	195.342	10.433	234.241	-5.085
1300	20.803	197.006	11.474	228.465	-3.798
1400	20.823	198.549	12.514	222.899	-2.790
1500	20.856	199.986	13.555	217.532	-2.041
1600	20.909	201.334	14.599	212.365	-1.491
1700	20.985	202.604	15.643	207.393	-1.113
1800	21.091	203.806	16.686	202.617	-0.861
1900	21.230	204.950	17.729	198.038	-0.703
2000	21.407	206.044	18.772	193.655	-0.594
2100	21.622	207.093	19.815	189.467	-0.519
2200	21.878	208.104	20.858	185.474	-0.463
2300	22.173	209.075	21.901	181.674	-0.424
2400	22.507	210.034	22.944	178.065	-0.399
2500	22.878	210.986	23.987	174.644	-0.385
2600	23.282	211.965	25.030	171.409	-0.381
2700	23.715	212.972	26.073	168.358	-0.385
2800	24.174	214.009	27.116	165.488	-0.394
2843.261	24.379	213.995	27.116	165.488	-0.394
2900	24.653	215.079	28.159	162.697	-0.408
3000	25.147	216.156	29.202	159.985	-0.433
3100	25.652	216.978	30.245	157.352	-0.468
3200	26.169	217.791	31.288	154.799	-0.513
3300	26.693	218.595	32.331	152.326	-0.567
3400	27.180	219.390	33.374	150.033	-0.630
3500	27.680	220.177	34.417	147.917	-0.703
3600	28.168	220.955	35.460	145.979	-0.786
3700	28.641	221.725	36.503	144.214	-0.879
3800	29.097	222.486	37.546	142.621	-0.982
3900	29.533	223.239	38.589	141.197	-1.094
4000	29.948	223.984	39.632	139.942	-1.215
4100	30.339	224.719	40.675	138.855	-1.344
4200	30.707	225.444	41.718	137.936	-1.481
4300	31.057	226.163	42.761	137.183	-1.626
4400	31.370	226.872	43.804	136.596	-1.779
4500	31.665	227.571	44.847	136.172	-1.939
4600	31.936	228.260	45.890	135.909	-2.106
4700	32.185	228.940	46.933	135.798	-2.280
4800	32.413	229.611	47.976	135.838	-2.461
4900	32.621	230.272	49.019	135.929	-2.649
5000	32.809	230.923	50.062	136.071	-2.844
5100	32.981	231.565	51.105	136.264	-3.046
5200	33.137	232.198	52.148	136.509	-3.255
5300	33.279	232.821	53.191	136.806	-3.471
5400	33.408	233.435	54.234	137.154	-3.694
5500	33.520	234.040	55.277	137.553	-3.934
5600	33.614	234.634	56.320	138.003	-4.190
5700	33.691	235.217	57.363	138.503	-4.463
5800	33.745	235.790	58.406	139.053	-4.754
5900	33.784	236.353	59.449	139.653	-5.064
6000	33.813	236.906	60.492	140.303	-5.394

PREVIOUS: June 1977 (1 atm)

CURRENT: September 1984 (1 bar)

Copper (Cu)

Cu₁(g)

Copper, Ion (Cu⁺)

IP(Cu⁺, g) = 163669.2 ± 0.5 cm⁻¹
 $S^\circ(298.15\text{ K}) = 222.311 \pm 0.02\text{ J K}^{-1}\text{ mol}^{-1}$

IDEAL GAS

$M_r = 63.54545$

Copper, Ion (Cu⁺)

$\Delta_f H^\circ(0\text{ K}) = 1081.9 \pm 2.1\text{ kJ mol}^{-1}$
 $\Delta_f H^\circ(298.15\text{ K}) = [1089.277]\text{ kJ mol}^{-1}$

Electronic Levels and Quantum Weights	$\epsilon_\infty, \text{cm}^{-1}$	g
$1S_0$	0.0	1
$3D_3$	21928.60	7
$3D_2$	22847.03	5
$3D_1$	23998.31	3
$1D_2$	26264.52	5

Enthalpy of Formation

$\Delta_f H^\circ(\text{Cu}^+, \text{g}, 0\text{ K})$ is calculated from $\Delta_f H^\circ(\text{Cu}, \text{g}, 0\text{ K})$ using the spectroscopic value of IP(Cu) = 62317.2 ± 0.5 cm⁻¹ (745.479 ± 0.006 kJ mol⁻¹) from Moore.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 Lias⁵ have summarized additional ionization and appearance potential data.

$\Delta_f H^\circ(\text{Cu}^+, \text{g}, 298.15\text{ K})$ is calculated from $\Delta_f H^\circ(\text{Cu}, \text{g}, 0\text{ K})$ by using IP(Cu) with JANAF¹ enthalpies, $H^\circ(0\text{ K}) - H^\circ(298.15\text{ K})$, for Cu(g), Cu⁺(g), and e⁻(g). $\Delta_f H^\circ(\text{Cu}^+, \text{g}, 298.15\text{ K})$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*⁴ $\Delta_f H^\circ(298.15\text{ K})$ 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 Moore,^{2,4} is incomplete because many theoretically predicted levels, that any reasonable method of filling in these missing levels and cutting off the summation in the partition function,⁷ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states. The next excited state is 66418.65 cm⁻¹ above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions to 6000 K, we list only the ground state and the first four excited states. The reported uncertainty in $S^\circ(298.15\text{ K})$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.⁷

References

- ¹JANAF Thermochemical Tables: Cu(g), 9-30-84; e⁻(ref), 3-31-82.
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Cu⁺(g)

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K			Standard State Pressure = P ^o = 0.1 MPa			log K _r
		J K ⁻¹ mol ⁻¹	S ^o	-(G ^o - H ^o (T _r))/T	H ^o - H ^o (T _r)	Δ _r H ^o	Δ _r G ^o	
0	0	0	0	INFINITE	-6.197	1081.889		
100	20.786	199.604	240.792		-4.119			-179.861
200	20.786	214.012	244.213		-2.040			-178.684
250	20.786	218.650	247.654		-1.001			-151.579
298.15	20.786	222.311	250.727		0	1089.277	1026.628	-131.235
300	20.786	222.440	250.856		0.038			-115.399
350	20.786	225.644	253.563		1.078			-102.722
400	20.786	228.420	255.127		2.117			-83.686
450	20.786	230.868	256.854		3.156			-70.070
500	20.786	233.038	258.667		4.196			-59.845
600	20.786	236.848	262.391		6.274			-51.881
700	20.786	240.052	266.119		8.353			-45.502
800	20.786	242.828	269.788		10.431			-40.277
900	20.786	245.276	273.376		12.510			-35.918
1000	20.786	247.466	276.877		14.589			-32.278
1100	20.786	249.447	280.295		16.667			-29.074
1200	20.786	251.256	283.634		18.746			-26.300
1300	20.786	252.919	286.901		20.824			-23.982
1400	20.786	254.460	290.100		22.903			-21.806
1500	20.786	255.894	293.239		24.982			-19.746
1600	20.786	257.235	296.323		27.060			-17.838
1700	20.786	258.495	299.354		29.139			-16.042
1800	20.786	259.684	302.341		31.217			-14.343
1900	20.786	260.807	305.283		33.296			-12.737
2000	20.786	261.874	308.186		35.375			-11.211
2100	20.786	262.888	311.053		37.453			-9.767
2200	20.786	263.855	313.886		39.532			-8.402
2300	20.786	264.779	316.687		41.610			-7.109
2400	20.786	265.663	319.450		43.689			-5.884
2500	20.786	266.512	322.182		45.768			-4.722
2600	20.786	267.327	324.895		47.846			-3.620
2700	20.786	268.112	327.581		49.925			-2.567
2800	20.786	268.868	330.245		52.004			-1.550
2900	20.786	269.597	332.888		54.082			-0.563
3000	20.786	270.302	335.511		56.161			0.403
3100	20.786	270.983	338.116		58.239			1.350
3200	20.786	271.643	340.704		60.318			2.297
3300	20.786	272.283	343.274		62.397			3.244
3400	20.787	272.903	345.830		64.475			4.191
3500	20.787	273.506	348.374		66.554			5.138
3600	20.787	274.091	350.907		68.633			6.085
3700	20.787	274.661	353.430		70.711			7.032
3800	20.787	275.215	355.944		72.790			7.979
3900	20.787	275.755	358.448		74.869			8.926
4000	20.788	276.282	360.945		76.948			9.873
4100	20.788	276.795	363.433		79.026			10.820
4200	20.788	277.296	365.916		81.105			11.767
4300	20.789	277.783	368.394		83.184			12.714
4400	20.789	278.263	370.868		85.263			13.661
4500	20.789	278.730	373.331		87.342			14.608
4600	20.790	279.187	375.786		89.421			15.555
4700	20.790	279.634	378.237		91.500			16.502
4800	20.791	280.072	380.684		93.579			17.449
4900	20.791	280.501	383.129		95.658			18.396
5000	20.792	280.921	385.574		97.737			19.343
5100	20.792	281.332	388.019		99.816			20.290
5200	20.793	281.736	390.464		101.895			21.237
5300	20.793	282.132	392.909		103.975			22.184
5400	20.794	282.521	395.354		106.054			23.131
5500	20.794	282.902	397.799		108.133			24.078
5600	20.795	283.277	400.244		110.213			25.025
5700	20.796	283.645	402.689		112.292			25.972
5800	20.796	284.007	405.134		114.372			26.919
5900	20.797	284.362	407.579		116.452			27.866
6000	20.798	284.712	410.024		118.531			28.813

PREVIOUS June 1977 (1 atm)

CURRENT, September 1984 (1 bar)

Cu⁺(g)Copper, Ion (Cu⁺)

Copper, Ion (Cu⁺)

IDEAL GAS

Cu⁺(g)

EA(Cu, g) = 1.228 ± 0.010 eV
 $S^{\circ}(298.15 \text{ K}) = 160.634 \pm 0.001 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 0 \text{ K}) = 217.926 \text{ kJ mol}^{-1}$
 $\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 298.15 \text{ K}) = [212.920] \text{ kJ mol}^{-1}$

Electronic level and quantum weight	
State	$\epsilon_e, \text{cm}^{-1}$
¹ S ₀	0.0
	1

Enthalpy of Formation

$\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 0 \text{ K})$ is calculated from $\Delta H_f^{\circ}(\text{Cu}, \text{g}, 0 \text{ K})$ using the adopted electron affinity of EA(Cu) = 1.228 ± 0.010 eV (118.483 ± 0.965 kJ mol⁻¹). This value, recommended by Hotoop and Lineberger,³ is based on a laser photodetachment electron spectroscopy study. Additional information on Cu⁺(g) may be obtained in the critical discussions of Hotoop and Lineberger,^{2,4} Rosenstock *et al.*,⁵ and Massey.⁶
 $\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 298.15 \text{ K})$ is obtained from $\Delta H_f^{\circ}(\text{Cu}, \text{g}, 0 \text{ K})$ by using EA(Cu) with JANAF enthalpies, $H^{\circ}(0 \text{ K}) - H^{\circ}(298.15 \text{ K})$, for Cu⁺(g), Cu(g), and e⁻(g). $\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 298.15 \text{ K})$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*,⁵ $\Delta H_f^{\circ}(\text{Cu}^+, \text{g}, 298.15 \text{ K})$ 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 electronic configuration for Cu⁺(g) is given by Hotoop and Lineberger^{2,4} and Rosenstock *et al.*,⁵ Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

- ¹JANAF Thermochemical Tables: Cu(g), 9-30-84, e⁻(ref), 3-31-82.
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- ⁶H. S. W. Massey, Negative Ions, 3rd ed., Cambridge University Press, Cambridge, (1976).

T/K	C _p ^o	Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p ^o = 0.1 MPa		log K _r
		J·K ⁻¹ ·mol ⁻¹	S ^o - [C _p ^o - H ^o (T _r)]/T	H ^o - H ^o (T _r)	ΔG ^o	
0	0	0	INFINITE	-6.197	217.926	
100	20.786	137.927	179.114	-4.119		
200	20.786	162.334	162.334	-2.040		
250	20.786	166.976	160.634	-1.001		
298.15	20.786	160.634	160.634	0		
300	20.786	160.762	160.834	0.038	212.874	181.169
350	20.786	163.967	160.687	1.078	212.874	180.972
400	20.786	166.742	161.450	2.117	210.381	175.753
450	20.786	169.190	162.176	3.156	209.105	170.712
500	20.786	171.381	162.989	4.196	207.815	165.830
600	20.786	175.170	164.713	6.274	205.195	161.091
700	20.786	178.714	166.442	8.353	202.521	151.991
800	20.786	181.130	168.111	10.431	199.797	143.334
900	20.786	183.598	169.698	12.510	197.020	135.064
1000	20.786	185.788	171.200	14.589	194.186	127.159
1100	20.786	187.769	172.617	16.667	191.281	119.525
1200	20.786	189.578	173.956	18.746	188.286	112.199
1300	20.786	191.242	175.223	20.824	185.158	105.141
1400	20.786	192.782	176.423	22.903	181.838	98.338
1500	20.786	194.216	177.562	24.982	168.742	92.189
1600	20.786	195.558	178.645	27.060	165.458	86.835
1700	20.786	196.818	179.677	29.139	162.173	81.701
1800	20.786	198.006	180.663	31.217	158.889	76.772
1900	20.786	199.130	181.606	33.296	155.605	72.036
2000	20.786	200.196	182.509	35.375	152.320	67.483
2100	20.786	201.210	183.375	37.453	149.036	63.103
2200	20.786	202.177	184.208	39.532	145.751	58.887
2300	20.786	203.101	185.010	41.610	142.467	54.828
2400	20.786	203.986	185.782	43.689	139.182	50.782
2500	20.786	204.834	186.527	45.768	135.898	46.751
2600	20.786	205.650	187.247	47.846	132.613	42.735
2700	20.786	206.434	187.943	49.925	129.329	38.729
2800	20.786	207.190	188.617	52.004	126.045	34.749
2900	20.786	207.919	189.270	54.082	122.760	30.798
3000	20.786	208.624	189.904	56.161	119.478	26.873
3100	20.786	209.306	190.519	58.239	116.193	22.972
3200	20.786	209.966	191.116	60.318	112.908	19.094
3300	20.786	210.605	191.697	62.397	109.623	15.235
3400	20.786	211.226	192.262	64.475	106.338	11.394
3500	20.786	211.828	192.813	66.554	103.053	7.562
3600	20.786	212.414	193.349	68.632	99.768	3.730
3700	20.786	212.983	193.872	70.711	96.483	-0.102
3800	20.786	213.538	194.386	72.790	93.198	-3.934
3900	20.786	214.078	194.881	74.868	89.913	-7.766
4000	20.786	214.604	195.367	76.947	86.628	-11.598
4100	20.786	215.117	195.843	79.025	83.343	-15.430
4200	20.786	215.618	196.308	81.104	80.058	-19.262
4300	20.786	216.107	196.762	83.183	76.773	-23.094
4400	20.786	216.585	197.207	85.261	73.488	-26.926
4500	20.786	217.052	197.643	87.340	70.203	-30.758
4600	20.786	217.509	198.070	89.418	66.918	-34.590
4700	20.786	217.956	198.489	91.497	63.633	-38.422
4800	20.786	218.394	198.897	93.576	60.348	-42.254
4900	20.786	218.822	199.301	95.654	57.063	-46.086
5000	20.786	219.242	199.696	97.733	53.778	-49.918
5100	20.786	219.654	200.083	99.811	50.493	-53.750
5200	20.786	220.057	200.463	101.890	47.208	-57.582
5300	20.786	220.453	200.837	103.969	43.923	-61.414
5400	20.786	220.842	201.203	106.047	40.638	-65.246
5500	20.786	221.223	201.564	108.126	37.353	-69.078
5600	20.786	221.598	201.918	110.204	34.068	-72.910
5700	20.786	221.966	202.267	112.283	30.783	-76.742
5800	20.786	222.327	202.610	114.362	27.498	-80.574
5900	20.786	222.682	202.947	116.440	24.213	-84.406
6000	20.786	223.032	203.279	118.519	20.928	-88.238

PREVIOUS

CURRENT: September 1984 (1 bar)

Copper, Ion (Cu⁺)Cu⁺(g)

Copper Fluoride (CuF)

CRYSTAL

$M_r = 82.544403$

Copper Fluoride (CuF)

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IDEAL GAS

 $M_r = 82.544403$

Copper Fluoride (CuF)

Cu₂F₂(g) $D_0 = 425.5 \pm 20.9 \text{ kJ mol}^{-1}$ $S^\circ(298.15 \text{ K}) = 226.495 \pm 0.21 \text{ J K}^{-1} \text{ mol}^{-1}$ $\Delta_f H^\circ(0 \text{ K}) = -12.22 \pm 16.7 \text{ kJ mol}^{-1}$ $\Delta_f H^\circ(298.15 \text{ K}) = -12.55 \pm 16.7 \text{ kJ mol}^{-1}$

Electronic levels and quantum weights	
State	g_r
X(¹ S)	0
A(¹ H)	17546.8
B(¹ S)	19738.5
C(¹ H)	20258.8

 $\omega_e x_e = 622.65 \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = 3.950 \text{ cm}^{-1}$ $r_e = 1.7449 \text{ \AA}$ $B_e = 0.3786 \text{ cm}^{-1}$ $\alpha_e = 0.0032 \text{ cm}^{-1}$

Enthalpy of Formation
Hildenbrand¹ and Ehlert and Wang² have reported mass spectrometric measurements of equilibrium pressures of the reactions $\text{MgF(g)} + \text{Cu(g)} = \text{Mg(g)} + \text{CuF(g)}$ and $1/2 \text{ CuF}_2(\text{cr}) + 1/2 \text{ CuF(g)} = \text{CuF(g)}$, respectively. Our 2nd and 3rd law analyses follow.

Source	Reaction*	77 K	Data points	$\Delta_f H^\circ(298.15 \text{ K})$, kcal mol ⁻¹	2nd law	3rd law	Drift	$\Delta_f H^\circ(298.15 \text{ K})$, kcal mol ⁻¹
1	A	1413-1590	12	11.57 ± 2.84	7.08 ± 0.68	-2.9 ± 1.9	-4.15 ± 3	
2	B	936-948	3	75.97 ± 3.90	62.34 ± 0.19	-14.5 ± 4.1	-2.06 ± 2.1	

*Reactions: (A) $\text{MgF(g)} + \text{Cu(g)} = \text{Mg(g)} + \text{CuF(g)}$
(B) $1/2 \text{ CuF}_2(\text{cr}) + 1/2 \text{ CuF(g)} = \text{CuF(g)}$

We adopt the rounded average, $\Delta_f H^\circ(\text{CuF, g, } 298.15 \text{ K}) = -3.0 \pm 4 \text{ kcal mol}^{-1}$ ($-12.552 \pm 16.7 \text{ kJ mol}^{-1}$), which leads to $D_0(\text{CuF, } 298.15 \text{ K}) = 102.5 \pm 5 \text{ kcal mol}^{-1}$ and $D_0(\text{CuF}) = 101.7 \pm 5 \text{ kcal mol}^{-1}$ ($425.513 \pm 20.9 \text{ kJ mol}^{-1}$).

Another value extant in the literature is $D_0(298.15 \text{ K}) = 83.6 \pm 4.0 \text{ kcal mol}^{-1}$ estimated from the heat of atomization of CuF₂, derived from sublimation studies, and the ratio $D_0(\text{Mg-F})/\Delta_f H^\circ(\text{MF}_2) = 0.46^3$. Hildenbrand¹ has discussed the valence state concept which predicts that $D_0(\text{Mg-F}) > D_0(\text{Mg-F}_2)$; therefore the ratio $D_0(\text{Mg-F})/D_0(\text{Mg-F}_2)$ must be greater than 0.5. With $\Delta_f H^\circ(\text{CuF}_2, 298.15 \text{ K}) = 182.17 \text{ kcal mol}^{-1}$ and $D_0(\text{CuF}, 298.15 \text{ K}) = -102.5 \text{ kcal mol}^{-1}$, the ratio based on JANAF values is 0.56. For $\Delta_f H^\circ(\text{CuF}_2, 298.15 \text{ K}) = 182.7 \text{ kcal mol}^{-1}$, $D_0(\text{CuF}, 298.15 \text{ K})$ must be greater than 91.08 kcal mol⁻¹ to agree with the valence state concept.

Other calculations by Kent *et al.*⁴ give $D_0(298.15 \text{ K})$ values ranging from 84.4 to 94.5 kcal mol⁻¹. Gaydon⁵ recommends $D_0^\circ = 81 \text{ kcal mol}^{-1}$ from a linear Birge-Sponer extrapolation of spectroscopic data but suggests that it is probably higher. King *et al.*⁶ used $\Delta_f H^\circ(298.15 \text{ K}) = 14 \text{ kcal mol}^{-1}$, $\Delta_f H^\circ(298.15 \text{ K}) = 84.7 \text{ kcal mol}^{-1}$ in their recent tabulation.

Heat Capacity and Entropy

The values of B_e and r_e are from the microwave data of Hoeft *et al.*⁷ adjusted for normal isotopic abundance; the electronic levels, ω_e , and $\omega_e x_e$ are taken from Rosen.⁸

References

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- JANAF Thermochemical Tables: MgF(g), 6-30-76; Mg(g), 9-30-62; Cu(cr, g), 6-30-77; CuF₂(cr, g), 12-31-77.
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T/K	C _p ^a	S ^b	-(G ^c -H ^c)/T	H ^c -H ^o (T)/T	Δ _f H ^o	log K _r
0	0	0	INFINITE	INFINITE	-12.216	INFINITE
100	29.204	192.900	254.629	-9.083	-12.216	-11.072
200	31.140	213.620	229.482	-6.173	-11.428	-8.049
250	32.375	220.704	227.040	-3.172	-11.905	-7.419
298.15	33.379	226.495	226.495	0	-12.552	-7.001
300	33.414	226.702	226.496	0.062	-12.564	-6.988
350	34.234	231.917	226.906	1.754	-12.903	-6.671
400	34.871	236.532	227.826	3.482	-13.248	-6.427
450	35.367	240.669	229.027	5.239	-13.600	-6.233
500	35.759	244.416	230.382	7.017	-13.961	-6.073
600	36.327	250.989	233.284	10.623	-14.712	-5.824
700	36.713	256.620	236.225	14.276	-15.508	-5.636
800	36.992	261.541	239.088	17.962	-16.351	-5.488
900	37.203	265.911	241.831	21.673	-17.245	-5.366
1000	37.371	269.840	244.438	25.402	-18.194	-5.263
1100	37.509	273.408	246.912	29.146	-19.215	-5.175
1200	37.627	276.677	249.258	32.903	-20.226	-5.097
1300	37.730	279.693	251.485	36.671	-21.231	-5.026
1400	37.822	282.493	253.601	40.448	-22.235	-4.947
1500	37.906	285.105	255.615	44.229	-23.238	-4.856
1600	37.984	287.554	257.536	48.029	-24.239	-4.773
1700	38.058	289.859	259.370	51.831	-25.237	-4.697
1800	38.129	292.036	261.125	55.641	-26.232	-4.627
1900	38.198	294.100	262.806	59.457	-27.224	-4.562
2000	38.267	296.061	264.421	63.280	-28.213	-4.502
2100	38.336	297.930	265.972	67.111	-29.200	-4.446
2200	38.408	299.715	267.466	70.948	-30.184	-4.393
2300	38.483	301.424	268.905	74.792	-31.165	-4.343
2400	38.564	303.063	270.294	78.645	-32.143	-4.297
2500	38.651	304.639	271.637	82.505	-33.119	-4.252
2600	38.746	306.157	272.936	86.375	-34.093	-4.211
2700	38.850	307.621	274.193	90.255	-35.066	-4.171
2800	38.965	309.036	275.413	94.143	-36.036	-4.133
2900	39.092	310.405	276.596	98.048	-37.003	-4.099
3000	39.233	311.732	277.745	101.964	-37.967	-4.074
3100	39.387	313.022	278.862	105.897	-38.928	-4.054
3200	39.556	314.275	279.949	109.844	-39.886	-4.038
3300	39.740	315.495	281.008	113.807	-40.841	-4.024
3400	39.940	316.684	282.040	117.791	-41.794	-4.010
3500	40.156	317.845	283.046	121.795	-42.744	-4.000
3600	40.387	318.980	284.029	125.822	-43.691	-3.993
3700	40.634	320.089	284.989	129.873	-44.634	-3.987
3800	40.896	321.177	285.927	133.950	-45.573	-3.982
3900	41.173	322.242	286.844	138.053	-46.508	-3.977
4000	41.464	323.288	287.742	142.183	-47.439	-3.972
4100	41.767	324.316	288.622	146.346	-48.366	-3.967
4200	42.083	325.326	289.484	150.539	-49.289	-3.962
4300	42.410	326.320	290.329	154.763	-50.209	-3.957
4400	42.746	327.299	291.158	159.021	-51.126	-3.952
4500	43.092	328.264	291.972	163.313	-52.040	-3.947
4600	43.445	329.215	292.771	167.640	-52.952	-3.942
4700	43.804	330.153	293.557	172.002	-53.861	-3.937
4800	44.168	331.079	294.329	176.400	-54.767	-3.932
4900	44.536	331.993	295.088	180.836	-55.670	-3.927
5000	44.907	332.897	295.835	185.308	-56.571	-3.922
5100	45.279	333.790	296.571	189.817	-57.469	-3.917
5200	45.651	334.673	297.295	194.364	-58.364	-3.912
5300	46.021	335.546	298.008	198.947	-59.256	-3.907
5400	46.390	336.409	298.712	203.568	-60.145	-3.902
5500	46.755	337.264	299.405	208.225	-61.032	-3.897
5600	47.115	338.110	300.088	212.919	-61.916	-3.892
5700	47.470	338.947	300.763	217.648	-62.797	-3.887
5800	47.819	339.775	301.428	222.412	-63.675	-3.882
5900	48.161	340.596	302.085	227.211	-64.550	-3.877
6000	48.496	341.408	302.734	232.044	-65.422	-3.872

PREVIOUS: December 1977 (1 atm)

CURRENT: December 1977 (1 bar)

Copper Fluoride (CuF)

Cu₂F₂(g)

Copper Fluoride (CuF₂)

CRYSTAL

Copper Fluoride (CuF₂)Cu₂F₂(cr)

$S^\circ(298.15\text{ K}) = 77.452 \pm 0.08\text{ J K}^{-1}\text{mol}^{-1}$
 $T_{\text{fus}} = 1109 \pm 10\text{ K}$
 $\Delta H_f^\circ(0\text{ K}) = -537.2 \pm 8.4\text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15\text{ K}) = -538.9 \pm 8.4\text{ kJ mol}^{-1}$
 $\Delta_{\text{ion}}H^\circ = 55.229 \pm 20.1\text{ kJ mol}^{-1}$

Enthalpy of Formation

Pervov *et al.*¹ have measured an enthalpy of formation of $-128.8 \pm 0.3\text{ kcal mol}^{-1}$ by direct fluorine combustion calorimetry. In view of the spread of values obtained from the equilibrium pressure and the emf data discussed below, we adopt $\Delta H_f^\circ(\text{CuF}_2, \text{cr}, 298.15\text{ K}) = -128.8 \pm 2\text{ kcal mol}^{-1}$ ($-538.899 \pm 8.4\text{ kJ mol}^{-1}$).

Jellinek and Rudat² and Domange³ have measured equilibrium partial pressures for reactions of CuF₂(cr) with hydrogen and with water, respectively. Koerber and De Vries⁴ and Skellon and Patterson⁵ have derived $\Delta_r G^\circ$ from emf studies. Our 2nd and 3rd law analyses are as follows, using auxiliary data from the JANAF Thermochemical Tables⁶.

Source	Reactions*	T/K	Data points	$\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹	2nd law	3rd law	Drift, cal K ⁻¹ mol ⁻¹	$\Delta H_f^\circ(298.15\text{ K})$, kcal mol ⁻¹
1	A	423	1	—	22.6	—	—	-152.9
2	B	573-723	4	23.3 ± 1.3	20.8 ± 0.6	—	-3.9 ± 2.0	-130.6 ± 2
3	C	273-283	2	-1.9	-10.6 ± 0.4	—	-31.4	-126.6 ± 4
4	D	661-918	Equation	-132.1	-136.4	—	-5.5	-136.4

*Reactions: (A) $\text{CuF}_2(\text{cr}) + \text{H}_2(\text{g}) = \text{Cu}(\text{cr}) + 2\text{HF}(\text{g})$
 (B) $\text{CuF}_2(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{CuO}(\text{cr}) + 2\text{HF}(\text{g})$
 (C) $\text{Cu}(\text{cr}) + \text{H}_2\text{F}_2 = \text{CuF}_2(\text{cr}) + 2\text{H}_2(\text{g})$
 (D) $\text{Cu}(\text{cr}) + \text{F}_2(\text{g}) = \text{CuF}_2(\text{cr})$

The evaluation of King *et al.*,⁷ $\Delta H_f^\circ(\text{CuF}_2, \text{cr}, 298.15\text{ K}) = -130.2\text{ kcal mol}^{-1}$, preceded the direct fluorination study of Pervov *et al.*¹ and is based mainly on the work of Domange³ and Koerber and De Vries.⁴ We place greater reliance on the direct fluorination work.¹

Heat Capacity and Entropy

The heat capacity is based on smoothed values from the unpublished low temperature measurements of Boo and Stout⁸ (10-300 K) and the differential scanning calorimetric measurements of heat capacity by Ehler⁹ (300-710 K). Our graphical joining and smoothing of the two data sets produces data which are 1 to 2% lower than Ehler's measurements⁹ in the 350-500 K range and are in agreement from 520-700 K; our extrapolation to 1000 K yields $21.60\text{ cal K}^{-1}\text{mol}^{-1}$ compared to $22.4\text{ cal K}^{-1}\text{mol}^{-1}$ by Ehler.⁹

Boo and Stout⁸ show an anomaly in the heat capacity at 70.90 K. $S^\circ(298.15\text{ K}) = 18.51\text{ cal K}^{-1}\text{mol}^{-1}$ is based on $S^\circ(10\text{ K}) = 0.009\text{ cal K}^{-1}\text{mol}^{-1}$ by Boo and Stout.⁸

Fusion Data

Ehler and Wang¹ interpret their DTA measurements as indicating a solid state transition at $1065 \pm 10\text{ K}$ and a fusion point of $1109 \pm 10\text{ K}$. They believe the observed transitions at 1028 K and 1040 K are caused by $\text{Cu}_2\text{O}-\text{CuF}_2$ and $10\text{ CuO} \cdot 70\text{ CuF}_2$ weight percent eutectics, respectively. Based on the latter, and ignoring the 1065 K solid state transition, they calculated an enthalpy of fusion of $13.2 \pm 2\text{ kcal mol}^{-1}$. We adopt $T_{\text{fus}} = 1109 \pm 10\text{ K}$ and $\Delta_{\text{fus}}H^\circ = 13.2 \pm 5\text{ kcal mol}^{-1}$ and await confirmation of the solid state transition.

Sublimation Data

Refer to the ideal gas table for details.

References

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PREVIOUS: June 1966

CURRENT: December 1977

Copper Fluoride (CuF₂)Cu₂F₂(cr)

	0 to above	1109 K 1109 K	crystal liquid
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Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa	
T/K	C_p°	$S^\circ - (G^\circ - H^\circ(T))/T$ $J \cdot K^{-1} \cdot mol^{-1}$	$H^\circ - H^\circ(T)$ $kJ \cdot mol^{-1}$
0	0	INFINITE	INFINITE
100	34.229	21.852	-537.170
200	55.731	53.151	-539.289
298.15	65.552	77.452	-539.591
300	65.689	77.858	-538.899
400	72.383	97.697	-538.881
500	77.739	114.446	-536.097
600	81.923	129.001	-534.201
700	84.810	141.857	-532.083
800	87.027	153.332	-529.821
900	88.868	163.692	-527.454
1000	90.374	173.136	-525.013
1100	91.588	181.807	-522.539
1109.000	91.713	182.554	-522.539
1109.000	100.416	232.354	-522.539
1200	100.416	240.273	-522.539
1300	100.416	248.111	-522.539
1400	100.416	255.753	-522.539
1500	100.416	262.681	-522.539
1600	100.416	269.161	-522.539
1700	100.416	275.249	-522.539
1800	100.416	280.989	-522.539
1900	100.416	286.418	-522.539
2000	100.416	291.568	-522.539
2100	100.416	296.468	-522.539
2200	100.416	301.139	-522.539
2300	100.416	305.603	-522.539
2400	100.416	309.876	-522.539
2500	100.416	313.976	-522.539
CRYSTAL $\leftarrow \rightarrow$ LIQUID			
TRANSITION			
			ΔG°
			$\log K$
			15.947
			14.298
			13.064
			11.896
			10.880
			9.989
			9.203
			8.503
			7.877
			7.315
			6.807
			6.346
			5.926
			5.542

PREVIOUS:

CURRENT: December 1977

Copper Fluoride (CuF₂)

Cu₁F₂(cr,l)

Cu₁F₂(g)Copper Fluoride (CuF₂)

CURRENT: December 1977 (1 bar)

PREVIOUS: December 1977 (1 atm)

Cu₁F₂(g)M_r = 101.542806 Copper Fluoride (CuF₂)

IDEAL GAS

Copper Fluoride (CuF₂)

$$\Delta H_f^\circ(0\text{ K}) = 265.16 \pm 12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ(298.15\text{ K}) = 266.94 \pm 12.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(298.15\text{ K}) = [267.09 \pm 2.1] \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Electronic Levels and Quantum Weights	
State	ϵ , cm ⁻¹
[Σ ⁺ _g]	0
[Π _g]	[9000]
[Δ _g]	[18000]
Vibrational Frequencies and Degeneracies	
ν, cm ⁻¹	
625 (1)	
185 ± 5 (1)	
782 (1)	

Ground State Quantum Weight: [2]

Point Group: C_{2v}

Bond Distance: Cu-F = [1.72] Å

Bond Angle: F-Cu-F = 165 ± 8°

Product of the Moments of Inertia: I_AI_BI_C = [6.77288 × 10¹⁶] g³·cm⁶

σ = 2

Enthalpy of Formation

Sublimation pressures, CuF₂(cr) = CuF₂(g), have been measured by Kent *et al.*¹ (897–1026 K) and by Ehler and Wang² (874–1005 K) by effusion cell mass spectrometric techniques. Using JANAF data³ for CuF₂(cr), we derive the following by 2nd and 3rd law analysis:

Source	T/K	Data points	Δ _{sub} H°(298.15 K), kcal·mol ⁻¹	Drift cal K ⁻¹ ·mol ⁻¹	ΔH _f °(g, 298.15 K), kcal·mol ⁻¹
¹	897–1026	26 ^a	63.20 ± 0.50	62.74 ± 0.17	-66.1
² via CuF*	874–1005	33 ^b	65.82 ± 0.72	64.997 ± 0.33	-63.8
² via CuF*	874–1005	33 ^b	65.92 ± 0.67	65.085 ± 0.30	-63.8

^aTwo data points eliminated by a statistical test.^bOne data point eliminated by a statistical test.We adopt ΔH_f°(CuF₂, g, 298.15 K) = -63.8 ± 3 kcal·mol⁻¹ (266.4 ± 12.6 kJ mol⁻¹).

Heat Capacity and Entropy

The bond distance is taken from Brewer *et al.*⁴ The bond distances for all of the transition metal difluorides from chromium through copper were estimated to be the same with the assessment that an error of 0.5 Å would lead to an error of less than 1 cal·K⁻¹·mol⁻¹ in the entropy. The bond angle and vibrational frequencies are those derived by Hastie *et al.*⁵ from infrared studies of matrix isolated isotopic species. The electronic states and levels are assumed the same as those assigned to CuCl₂.⁶ The principal moments of inertia are I_A = 0.1990 × 10⁻³⁹, I_B = 18.3484 × 10⁻³⁹, I_C = 18.5474 × 10⁻³⁹ g·cm².

References

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Enthalpy Reference Temperature = T _r = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
T/K	C _p ^a	S° - (G° - H°(T _r)/T)	log K _t
0	0	INFINITE	INFINITE
100	38.109	220.861	-265.163
200	43.318	248.878	-266.246
300	45.838	258.822	-266.117
400	47.987	267.086	-266.552
500	48.061	267.384	-266.939
600	48.359	267.679	-267.279
700	48.687	267.966	-267.579
800	49.041	268.246	-267.837
900	49.418	268.511	-268.055
1000	49.818	268.762	-268.233
1100	50.241	269.000	-268.371
1200	50.687	269.225	-268.478
1300	51.156	269.438	-268.555
1400	51.648	269.639	-268.603
1500	52.164	269.828	-268.632
1600	52.705	270.005	-268.643
1700	53.272	270.170	-268.637
1800	53.866	270.324	-268.613
1900	54.487	270.468	-268.571
2000	55.136	270.602	-268.513
2100	55.814	270.726	-268.440
2200	56.522	270.840	-268.355
2300	57.261	270.945	-268.259
2400	58.032	271.041	-268.153
2500	58.836	271.128	-268.038
2600	59.674	271.207	-267.914
2700	60.547	271.278	-267.782
2800	61.456	271.341	-267.643
2900	62.403	271.396	-267.498
3000	63.489	271.443	-267.348
3100	64.616	271.482	-267.193
3200	65.785	271.513	-267.034
3300	66.998	271.536	-266.871
3400	68.257	271.551	-266.705
3500	69.564	271.558	-266.537
3600	70.921	271.558	-266.367
3700	72.330	271.550	-266.195
3800	73.793	271.534	-266.021
3900	75.313	271.509	-265.846
4000	76.893	271.476	-265.670
4100	78.536	271.435	-265.493
4200	80.246	271.387	-265.316
4300	82.026	271.332	-265.139
4400	83.870	271.270	-264.962
4500	85.782	271.201	-264.785
4600	87.766	271.126	-264.608
4700	89.826	271.045	-264.431
4800	91.966	270.958	-264.254
4900	94.190	270.865	-264.077
5000	96.502	270.767	-263.900
5100	98.906	270.664	-263.723
5200	101.407	270.556	-263.546
5300	103.910	270.443	-263.369
5400	106.420	270.325	-263.192
5500	108.942	270.202	-263.015
5600	111.481	270.075	-262.838
5700	114.034	269.944	-262.661
5800	116.606	269.809	-262.484
5900	119.194	269.670	-262.307
6000	121.804	269.527	-262.130

Copper Hydroxide (Cu(OH)₂)

CRYSTAL

M_r = 97.56068Copper Hydroxide (Cu(OH)₂)Cu₂H₂O₂(cr)

$$S^{\circ}(298.15 \text{ K}) = [108.366] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_f H^{\circ}(298.15 \text{ K}) = -450.37 \pm 8.4 \text{ kJ mol}^{-1}$$

T/K	C _p ^a	Enthalpy Reference Temperature = T _r = 298.15 K			Standard State Pressure = p ^o = 0.1 MPa		
		J·K ⁻¹ ·mol ⁻¹	S ^o	-(G ^o - H ^o (T _r))/T	H ^o - H ^o (T _r)	Δ _f H ^o	log K _r

Enthalpy of Formation

The enthalpy change, Δ_fH^o(433 K), for the reaction Cu(OH)₂(cr) = CuO(cr) + H₂O(g) has been determined by My¹. Based on the reported value, Δ_fH^o(433 K) = 12 kcal·mol⁻¹. The adopted Δ_fH^o(Cu(OH)₂, cr, 298.15 K) value was derived as -107.64 kcal·mol⁻¹, using Δ_fH^o(298.15 K) = -37.250 and -57.798 kcal·mol⁻¹ for CuO(cr) and H₂O(g), respectively.

The Gibbs energy change, Δ_fG^o(298.15 K), of the reaction Cu(OH)₂(cr) = Cu²⁺(aq) + 2 OH⁻(aq) was evaluated to be 26.36 and 26.26 kcal·mol⁻¹, based on the solubility product for Cu(OH)₂(cr) reported by Ganelina² and Zhuk³, respectively. Using values of S^o(298.15 K) and Δ_fH^o(298.15 K) for Cu²⁺(aq) and OH⁻(aq) from NBS⁴ and NBS⁵, the corresponding enthalpy change Δ_fH^o(298.15 K) and enthalpy of formation, Δ_fH^o(298.15 K) for Cu(OH)₂(cr) are derived. The results obtained are presented as follows:

Reaction	Δ _f H ^o (298.15 K) kcal·mol ⁻¹	Δ _f H ^o (298.15 K) kcal·mol ⁻¹	Source
Cu(OH) ₂ (cr) = Cu ²⁺ (aq) + 2 OH ⁻ (aq)	10.06	-104.61	1
Cu(OH) ₂ (cr) = Cu ²⁺ (aq) + 2 OH ⁻ (aq)	9.97	-104.52	2
CuO(cr) + H ₂ O(l) = Cu(OH) ₂ (cr)	-1.9	-107.5	3
CuO(cr) + H ₂ O(l) = Cu(OH) ₂ (cr)	0.3	-105.3	4

The enthalpies of solution of CuO(cr) and Cu(OH)₂(cr) in HNO₃(aq) have been determined by de Forcrand⁶ to be -16.38 and -14.46 kcal·mol⁻¹, respectively. From these data, the enthalpy change for the reaction CuO(cr) + H₂O(l) = Cu(OH)₂(cr) was derived as -1.9 kcal·mol⁻¹. For the same reaction, the enthalpy change was reported to be 0.3 kcal·mol⁻¹ by Sabatier⁷. Based on Δ_fH^o(298.15 K) = -37.25 and -68.315 kcal·mol⁻¹ for CuO(cr) and H₂O(l), respectively, the enthalpy of formation for Cu(OH)₂ was evaluated. The results obtained are presented in the above table.

Heat Capacity and Entropy

Heat capacities, 298.15–700 K, were estimated by comparison with those for CuO(cr), CuO(cr) and Ca(OH)₂(cr). The C_p^o values above 700 K were obtained by graphical extrapolation. S^o(298.15 K) was estimated such that the derived Δ_fG^o(Cu(OH)₂, cr) = Δ_fG^o(CuO, cr) + Δ_fG^o(H₂O, g) at 433 K.

Decomposition Data

T_{de} = 433 K is the temperature at which the Gibbs energy change for the reaction Cu(OH)₂(cr) = CuO(cr) + H₂O(g) is such that the fugacity of water is 1 atm.

References

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PREVIOUS.

CURRENT June 1966

Copper Hydroxide (Cu(OH)₂)Cu₂H₂O₂(cr)

Copper Oxide (CuO)

CRYSTAL

 $M_r = 79.5454$ Copper Oxide (CuO) $\text{Cu}_2\text{O}(\text{cr})$

$S^\circ(298.15 \text{ K}) = 42.59 \pm 0.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $\Delta H_f^\circ(0 \text{ K}) = -153.81 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -156.06 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation of $\text{CuO}(\text{cr})$ has been investigated calorimetrically (both oxidation and reduction reactions) and by extensive study of the $\text{Cu}_2\text{O}(\text{cr}) + 1/2 \text{O}_2(\text{g}) = 2 \text{CuO}(\text{cr})$ equilibrium by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

Source	Method	Reaction*	T/K	Data points	$\Delta H_f^\circ(298.15 \text{ K})$, kcal·mol ⁻¹	2nd law	3rd law	Drift	$\Delta H_f^\circ(298.15 \text{ K})^{**}$, kcal·mol ⁻¹
1	Aq Calorim	A	291	—	31.15	—	—	—	-37.16
2	Calorimetric	A	295	—	30.27 ± 0.2	—	—	—	-38.04
3	Calorimetric	See Text	298.15	—	—	—	—	—	-37.23 ± 0.15
4	Calorimetric	A	297.9	(Coarse grain CuO)	—	—	—	—	-38.72 ± 0.30
		A	298	(Fine powder CuO)	—	—	—	—	-36.50 ± 0.2
		B	297.9	(Coarse grain CuO)	—	—	—	—	-38.59 ± 0.35
5	Equil Press	B	1011–1156	5	-33.84 ± 0.31	-37.73 ± 0.43	-3.6 ± 0.3	-37.73	-37.16
6	emf	B	845–1270	Equation	-37.26	-37.38	-0.1 ± 0.0	-37.38	-37.38
7	Equil Press	C	1223–1322	7	-32.52 ± 0.18	-33.65 ± 0.06	-0.9 ± 0.1	-37.23	-37.23
8	Equil Press	C	1189–1358	20	-33.28 ± 0.06	-33.68 ± 0.04	-0.3 ± 0.0	-37.24	-37.24
9	Equil Press	C	1193–1293	6	-33.23 ± 0.28	-33.68 ± 0.04	-0.4 ± 0.2	-37.24	-37.24
10	Equil Press	C	1047–1342	11	-32.79 ± 0.14	-33.69 ± 0.17	-0.7 ± 0.1	-37.25	-37.25
11	Equil Press	C	1026–1072	3	-35.50 ± 0.37	-33.62 ± 0.07	1.4 ± 0.3	-37.21	-37.21
12	emf	C	973–1273	Equation	-33.57	-33.64	-0.6	-37.22	-37.22
13	emf	C	892–1320	Equation	-33.53	-33.58	-0.6	-37.19	-37.19
14	emf	C	1023–1294	Equation	-33.39	-33.58	0.2	-37.19	-37.19
15	emf	C	870–1170	Equation	-34.37	-35.00	0.6	-37.90	-37.90
16	Press	C	993–1021	4	-34.18 ± 0.06	-34.12 ± 0.0	-0.1 ± 0.1	-37.46	-37.46
17	Equil Press	C	800–950	Equation	-29.92	-34.30	10.0	-37.55	-37.55
18	Equil Press	C	873–1073	Equation	-40.06	-35.26	4.9	-38.03	-38.03

*Reactions: (A) $\text{Cu}(\text{cr}) + \text{H}_2\text{O}(\text{l}) = \text{CuO}(\text{cr}) + \text{H}_2(\text{g})$ **Based on third law where possible and $\Delta H_f^\circ(\text{Cu}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -40.8 \text{ kcal} \cdot \text{mol}^{-1}$ in Reaction C.

(B) $\text{Cu}(\text{cr}) + 1/2 \text{O}_2(\text{g}) = \text{CuO}(\text{cr})$

(C) $\text{Cu}_2\text{O}(\text{cr}) + 1/2 \text{O}_2(\text{g}) = 2 \text{CuO}(\text{cr})$

Thomsen's data¹ may be reduced to the enthalpy of reduction of $\text{CuO}(\text{cr})$ with H_2 by combining enthalpies of reaction for $\text{CuO} + \text{H}_2\text{SO}_4$, $\text{Fe} + \text{H}_2\text{SO}_4$, and $\text{Fe} + \text{CuSO}_4(\text{aq})$. Wartenberg and Werth² and Nunez *et al.*³ have measured the direct enthalpy of reduction of $\text{CuO}(\text{cr})$ by H_2 ; Mah *et al.*³ and Nunez *et al.*⁴ have measured the direct enthalpy of oxidation of copper by O_2 . Mah *et al.*³ obtained a mixed Cu_2O and CuO product and used $\Delta H_f^\circ(298.15 \text{ K}) = -33.63 \pm 0.05 \text{ kcal} \cdot \text{mol}^{-1}$ for the equilibrium reaction $\text{Cu}_2\text{O}(\text{cr}) + 1/2 \text{O}_2(\text{g}) = 2 \text{CuO}(\text{cr})$ to resolve their results into $\Delta H_f^\circ(\text{CuO}, \text{cr}, 298.15 \text{ K})$ and $\Delta H_f^\circ(\text{Cu}_2\text{O}, \text{cr}, 298.15 \text{ K})$. From the measurement of the reduction of coarse and fine $\text{CuO}(\text{cr})$, Nunez *et al.*⁴ conclude that ΔH_f° of the copper oxides is influenced by material history, state of subdivision, and non stoichiometry.

Eliminating three studies^{1,17,18} from our 3rd law analysis because of large drift and poor 2nd and 3rd law agreement, the average of the eleven remaining studies is $-37.32 \text{ kcal} \cdot \text{mol}^{-1}$. We adopt $\Delta H_f^\circ(298.15 \text{ K}) = -37.3 \pm 0.5 \text{ kcal} \cdot \text{mol}^{-1}$.

Heat Capacity and Entropy

The adopted values are based on the low temperature heat capacities by Hu and Johnston¹⁹ (15–297 K) and the high temperature enthalpies by Mah *et al.*³ (410–1400 K). Changes are made where appropriate to adjust to the 1975 atomic weights²⁰ and the IPTS 68 temperature scale²¹. A small anomaly in the heat capacity was observed in the 210–230 K region. Magnetic measurements of O'Keefe and Stone²² and neutron diffraction studies of Brockhouse²³ suggest that this is a Neel point associated with antiferromagnetism.

The entropy is obtained from the adopted heat capacities based on a T^3 extrapolation to obtain $S^\circ(15 \text{ K}) = 0.016 \text{ cal} \cdot \text{K}^{-1}$.

Decomposition Data

$T_{\text{dec}} = 1397 \text{ K}$ is the temperature at which fugacity (O_2) = 1 atm for the reaction $2 \text{CuO}(\text{cr}) = \text{Cu}_2\text{O}(\text{cr}) + 1/2 \text{O}_2(\text{g})$.

References

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Continued on page 1027

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$				Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$			
T/K	C_p°	$S^\circ - [G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG°	log K _r	
0	0	0	INFINITE	-7.092	-153.807	INFINITE	
100	16.499	9.768	74.176	-6.441	-146.585	76.568	
200	34.795	27.018	46.256	-3.848	-137.461	35.901	
298.15	42.246	42.594	42.594	0	-128.292	22.476	
300	42.364	42.856	42.595	0.078	-128.120	22.308	
400	46.806	55.723	44.319	4.562	-118.875	15.523	
500	49.261	66.451	47.703	9.374	-109.785	11.469	
600	50.935	75.588	51.608	14.388	-100.851	8.780	
700	52.240	83.541	55.614	19.540	-92.056	6.869	
800	53.349	90.591	59.554	24.829	-83.387	5.445	
900	54.340	96.932	63.361	30.215	-74.830	4.343	
1000	55.262	102.706	67.011	35.695	-66.375	3.467	
1100	56.135	108.014	70.500	41.265	-58.012	2.755	
1200	56.978	112.935	73.834	46.921	-49.730	2.165	
1300	57.800	117.528	77.020	52.660	-41.520	1.668	
1400	58.601	121.841	80.069	58.480	-33.293	1.250	
1500	59.395	125.911	82.991	64.380	-25.899	0.832	
1600	60.181	129.769	85.795	70.359	-18.891	0.486	
1700	60.958	133.441	88.491	76.416	-12.938	0.182	
1800	61.726	136.947	91.086	82.550	-7.958	-0.086	
1900	62.494	140.305	93.589	88.761	-3.968	-0.324	
2000	63.259	143.530	96.006	95.049	0.049	-0.537	

PREVIOUS: June 1966

CURRENT: December 1977

Copper Oxide (CuO)

 $\text{Cu}_2\text{O}(\text{cr})$

Cu₂O(g)

Copper Oxide (CuO)

M_r = 79.5454

IDEAL GAS

Copper Oxide (CuO)

$$\Delta_f H^\circ(0 \text{ K}) = 305.87 \pm 41.8 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = 306.27 \pm 41.8 \text{ kJ mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = 234.617 \text{ J K}^{-1} \text{ mol}^{-1}$$

Electronic levels and quantum weights	ϵ , cm ⁻¹	g
X ² Π _{1/2}	0	2
X ² Π _{3/2}	277.0	2
A ² Σ ⁺	15531.9	2
A ² Σ ⁺	16492.4	2
C ² Π ₁	18811.4	4
E ² Δ ₂	21103.7	4
F ² Π ₁	21222	4
G ² Σ ⁻	21594.0	2
M ² Π _{1/2}	23898	4

$$\omega_e x_e = 640.14 \text{ cm}^{-1}$$

$$B_e = 0.44454 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\tau_e = 1.7246 \text{ Å}$$

Enthalpy of Formation

The adopted $\Delta_f H^\circ(298.15 \text{ K}) = 73.2 \pm 10 \text{ kcal mol}^{-1}$ comes from our 3rd law analysis of the mass spectrometric Knudsen cell measurements of the equilibrium reaction $\text{CuO(g)} + \text{Ni(g)} = \text{Cu(g)} + \text{NiO(g)}$ [1611–1828 K]. Auxiliary data^{2,3} are used in the analysis. Also considered in the evaluation are the unpublished but quoted⁴ and others] value of Burns, $D_0^\circ = 62.7 \pm 3 \text{ kcal mol}^{-1}$, the sublimation measurement of⁵, the linear Birge Sponer extrapolation of the ground state to obtain D_0° , and the linear Birge Sponer extrapolation corrected for the ionic character of CuO according to Hildenbrand.⁶

Source	$D_0^\circ(0 \text{ K})$ kcal mol ⁻¹	$\Delta_f H^\circ(298.15 \text{ K})$ kcal mol ⁻¹
Smoes <i>et al.</i> ¹ , Equilibrium	66.3	73.2
Burns ⁴ , Mass spec.	62.7 ± 3	76.8 ± 3
Mack <i>et al.</i> ⁵ , Transpiration (1273 K)	80.2	59.02
Linear Birge Sponer	65.2	74.2
Modified Linear Birge Sponer	61.0 ± 12	78.5 ± 12

Mack *et al.*⁵ report measurements at 873, 1073, and 1173 K which lead to higher dissociation energies. Because of the scatter of the measurements and the suspect nature of the analytical measurement recognized by the authors, the D_0° value of 80.2 kcal mol⁻¹ is discounted.

Heat Capacity and Entropy

The molecular constants and electronic levels are taken from the work of Appelblad and Lagerqvist,^{7,8,9} Lefebvre *et al.*,¹⁰ and Lefebvre *et al.*¹¹ The spectrum of CuO is complex and there are almost certainly excited states missing among those already analyzed,⁹ in fact some doubt still exists that the X²Π_{1/2} state is really the ground state⁹ although the absence of ev signals in the matrix isolation study of Thompson *et al.*¹² supports this assignment. Because of the uncertain and incomplete spectral analysis, we choose to calculate the thermodynamic functions with first order anharmonic corrections assuming the ground state vibrational rotational constants for all states. Use of the actual constants for each state increases the entropy at 6000 K by 0.045 cal K⁻¹ mol⁻¹.

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T/K	C _p J K ⁻¹ mol ⁻¹	S ^o - [C _p - H ^o (T)]/T J K ⁻¹ mol ⁻¹	H ^o - H ^o (T) kJ mol ⁻¹	Standard State Pressure = p ^o = 0.1 MPa Δ _f H ^o kJ mol ⁻¹	log K _r
0	0	0	INFINITE	305.866	INFINITE
100	31.554	197.630	-6.781	306.715	-154.919
200	34.498	220.596	-237.849	306.577	-74.840
250	35.198	228.373	-235.202	306.428	-58.829
298.15	35.693	234.617	0	306.269	-48.492
300	35.710	234.838	0.066	306.262	-48.161
350	36.098	240.373	1.862	306.083	-40.545
400	36.399	245.214	3.674	305.891	-34.837
450	36.636	249.515	5.501	305.683	-30.400
500	36.827	253.386	7.337	305.459	-26.853
600	37.114	260.127	11.035	304.957	-21.539
700	37.320	265.864	14.782	304.378	-17.479
800	37.478	270.858	18.498	303.746	-14.913
900	37.608	275.280	22.252	303.061	-12.712
1000	37.715	279.248	26.018	302.202	-10.956
1100	37.810	282.847	29.795	301.319	-9.523
1200	37.896	286.141	33.580	300.335	-8.332
1300	37.975	289.178	37.374	299.209	-7.328
1400	38.050	291.995	41.175	297.958	-6.486
1500	38.121	294.622	44.983	296.599	-5.780
1600	38.189	297.085	48.799	295.178	-5.164
1700	38.256	299.402	52.621	293.681	-4.623
1800	38.322	301.590	56.450	292.125	-4.145
1900	38.389	303.664	60.286	290.517	-3.719
2000	38.456	305.635	64.128	288.875	-3.337
2100	38.526	307.513	67.977	287.205	-2.994
2200	38.597	309.307	71.833	285.515	-2.683
2300	38.671	311.024	75.697	283.809	-2.400
2400	38.760	312.672	79.569	282.090	-2.143
2500	38.850	314.256	83.449	280.377	-1.907
2600	38.949	315.782	87.339	278.666	-1.690
2700	39.056	317.254	91.239	276.963	-1.491
2800	39.174	318.676	95.151	275.271	-1.306
2900	39.303	320.053	99.074	273.593	-1.134
3000	39.444	321.388	103.012	271.940	-1.000
3100	39.598	322.684	106.964	270.315	-0.885
3200	39.766	323.944	110.932	268.727	-0.785
3300	39.949	325.170	114.918	267.175	-0.697
3400	40.145	326.366	118.922	265.663	-0.621
3500	40.357	327.532	122.947	264.193	-0.558
3600	40.583	328.672	126.994	262.765	-0.506
3700	40.824	329.787	131.064	261.378	-0.464
3800	41.079	330.880	135.159	260.032	-0.430
3900	41.348	331.950	139.280	258.725	-0.400
4000	41.631	333.000	143.429	257.456	-0.374
4100	41.926	334.032	147.607	256.225	-0.351
4200	42.234	335.046	151.815	255.032	-0.330
4300	42.552	336.043	156.054	253.875	-0.311
4400	42.881	337.025	160.326	252.753	-0.294
4500	43.220	337.993	164.631	251.665	-0.279
4600	43.566	338.947	168.970	250.610	-0.265
4700	43.920	339.887	173.344	249.587	-0.252
4800	44.279	340.816	177.754	248.596	-0.240
4900	44.644	341.732	182.200	247.636	-0.229
5000	45.012	342.638	186.683	246.705	-0.219
5100	45.383	343.533	191.203	245.803	-0.210
5200	45.756	344.418	195.750	244.929	-0.201
5300	46.129	345.293	200.334	244.082	-0.193
5400	46.501	346.159	204.956	243.261	-0.185
5500	46.872	347.015	209.604	242.465	-0.178
5600	47.240	347.863	214.280	241.694	-0.171
5700	47.604	348.703	218.985	240.947	-0.164
5800	47.964	349.534	223.719	240.224	-0.158
5900	48.319	350.357	228.481	239.524	-0.152
6000	48.667	351.172	233.248	238.846	-0.146

PREVIOUS: December 1977 (1 atm)

CURRENT: December 1977 (1 bar)

Cu₂O(g)

Copper Oxide (CuO)

Copper Sulfate (CuSO₄)M_r = 159.6036 Copper Sulfate (CuSO₄)Cu₂O₄S₁(cr)
 $S^{\circ}(298.15\text{ K}) = 109.254 \pm 0.42\text{ J K}^{-1}\text{mol}^{-1}$
 $\Delta_f H^{\circ}(0\text{ K}) = -760.059 \pm 0.84\text{ kJ mol}^{-1}$
 $\Delta_f H^{\circ}(298.15\text{ K}) = -769.982 \pm 0.84\text{ kJ mol}^{-1}$

Enthalpy of Formation

The enthalpy of solution, $\Delta_f H^{\circ}(298.15\text{ K})$, of CuO(cr) in sulfuric acid to form CuSO₄(cr) has been measured by Adami and King.¹ From the reported value, $\Delta_f H^{\circ} = 5.61 \pm 0.09\text{ kcal mol}^{-1}$ for the reaction $\text{CuO(cr)} + \text{H}_2\text{SO}_4 \cdot 7.068\text{ H}_2\text{O(aq)} = \text{CuSO}_4\text{(cr)} + 8.068\text{ H}_2\text{O(l)}$, the enthalpy of formation, $\Delta_f H^{\circ}(298.15\text{ K})$, for CuSO₄(cr) was evaluated as $-184.03\text{ kcal mol}^{-1}$, using $\Delta_f H^{\circ}(298.15\text{ K}) = -37.25$, -209.49 and $-68.315\text{ kcal mol}^{-1}$ for CuO(cr), H₂SO₄·7.068 H₂O(aq) and H₂O(l), respectively. See Fe₂(SO₄)₃(cr) table for the sources of the last two $\Delta_f H^{\circ}(298.15\text{ K})$ values.

The equilibrium pressure for the following chemical reactions: (A) 2 CuSO₄(cr) = CuO·CuSO₄(cr) + SO₃(g), (B) 3 Cu(cr) + CuSO₄(cr) = 2 Cu₂O(cr) + SO₂(g), and (C) 4 CuSO₄(cr) + Cu₂O(cr) = 3 CuO·CuSO₄(cr) + SO₂(g), were determined by several investigators. For reaction (A), the partial pressures of SO₃(g) at different temperatures were calculated from the measured total pressures exerted by SO₃(g), SO₂(g) and O₂(g), produced by the reaction SO₃(g) = SO₂(g) + 1/2 O₂(g). From these vapor pressure data, the corresponding enthalpy changes, $\Delta_f H^{\circ}(298.15\text{ K})$, for the three reactions were evaluated by the 2nd and 3rd law methods. The results obtained are presented in the following table. The value of $\Delta_f H^{\circ}(\text{CuSO}_4, \text{cr}, 298.15\text{ K})$ adopted was $-184.03 \pm 0.2\text{ kcal mol}^{-1}$.

Source	Reaction	T/K	$\Delta_f H^{\circ}(298.15\text{ K}), \text{kcal mol}^{-1}$	2nd law	3rd law	Drift	$\Delta_f H^{\circ}(298.15\text{ K})$ kcal mol ⁻¹
²	(A)	819.15–1004.15		25.90 ± 3.60	47.45	22 ± 4	-181.87
³	(A)	953.15–1053.15		56.54 ± 0.77	51.96	-4.55 ± 0.79	-184.13
⁴	(C)	825.15–921.15		42.84 ± 1.38	42.34	-0.55 ± 1.57	-184.42
⁴	(B)	880.15–1071.75		51.59 ± 0.41	51.75	0.07 ± 0.43	-184.02
⁵	(A)	525.1 – 608.1		31.71 ± 0.76	32.27	0.84 ± 1.30	-184.62

Heat Capacity and Entropy

Low temperature heat capacities, 52.67–296.29 K, were obtained from Weller,⁶ The high temperature heat capacities were measured by Schottky⁷ (282°C), Ewald⁸ (275–373 K), Krestovnikov and Feigina⁹ (288–873 K), and Chiznikov and Khirik¹⁰ (373–1273 K). The heat capacities below 51 K were obtained from Stout.¹¹ In that paper, the C_p° values, 15–58 K, were plotted as function of temperature and the C_p° curve shows a maximum at 34.8 K. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve was drawn. The entropy above the normal C_p° curve is reported to be 0.48 cal K⁻¹mol⁻¹ rather than a magnetic entropy of Rln2 = 1.377 cal K⁻¹mol⁻¹. Apparently the magnetic entropy increases gradually above 40 K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

The C_p° values above 298.15 K were extrapolated smoothly by comparison with those for MnSO₄(cr) (refer to FeSO₄(cr) table for details). The adopted C_p° values are close to the average of the reported C_p° values.

The value of $S^{\circ}(298.15\text{ K})$ was derived using the low temperature C_p° data reported by Weller,⁶ based on $S^{\circ}(51\text{ K}) = 2.851\text{ cal K}^{-1}\text{mol}^{-1}$ evaluated from C_p° data determined by Stout.¹¹

Decomposition Data

$T_{\text{dec}} = 1078\text{ K}$ is the temperature at which the total pressure of the gaseous decomposition products equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for CuSO₄(cr), determined by Ingraham.⁴

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Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure = p° = 0.1 MPa	
T/K	C_p°	$S^{\circ} - [G^{\circ} - H^{\circ}(T)]/T$	$\Delta_f H^{\circ}$
0	0	0	-760.059
100	43.718	32.670	-760.059
200	71.008	74.167	-760.059
298.15	98.868	109.254	-760.059
300	99.286	109.867	-760.059
400	114.934	140.654	-760.059
500	127.194	167.676	-760.059
600	136.315	191.710	-760.059
700	142.925	213.244	-760.059
800	147.695	232.656	-760.059
900	151.042	250.251	-760.059
1000	153.762	266.369	-760.059
1100	156.063	281.074	-760.059
1200	158.113	294.743	-760.059
1300	159.954	307.473	-760.059
1400	161.628	319.388	-760.059
1500	163.218	330.594	-760.059
1600	164.724	341.177	-760.059
1700	166.147	351.206	-760.059
1800	167.569	360.743	-760.059
1900	168.908	369.839	-760.059
2000	170.247	378.537	-760.059
$H^{\circ} - H^{\circ}(T_i)$			
			-16.863
			-14.875
			-8.696
			0
			0.183
			10.923
			21.055
			36.251
			50.229
			64.772
			79.714
			94.938
			110.451
			126.161
			142.066
			158.146
			174.335
			190.787
			207.437
			224.017
			240.841
			257.798
$\Delta_f G^{\circ}$			
			-760.059
			-731.589
			-696.504
			-660.781
			-623.342
			-586.042
			-548.744
			-511.625
			-474.730
			-437.054
			-394.741
			-352.795
			-311.188
			-269.891
			-228.471
			-186.755
			-145.290
			-104.068
			-63.079
			-22.313
			18.236

PREVIOUS:

CURRENT: June 1966

Copper Sulfate (CuSO₄)Cu₂O₄S₁(cr)

Copper (Cu₂)Copper (Cu₂)

IDEAL GAS

Cu₂(g)

$$\Delta H_f^\circ(0 \text{ K}) = 1485.43 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_f^\circ(298.15 \text{ K}) = 485.34 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$S^\circ(298.15 \text{ K}) = 241.72 \text{ J K}^{-1} \cdot \text{mol}^{-1}$$

Electronic Levels and Quantum Weights	
State	g_e
$[\Sigma_g^+]$	0
	20433
	21758
	$[\Pi]$
	$[\Pi]$
	$[\Pi]$

$$\sigma = 2$$

$$r_e = 2.219 \text{ \AA}$$

$$\omega_e x_e = 1.015 \text{ cm}^{-1}$$

$$\alpha_e = 0.000608 \text{ cm}^{-1}$$

$$\omega_e = 265.34 \text{ cm}^{-1}$$

$$B_e = 0.10776 \text{ cm}^{-1}$$

Enthalpy of Formation

The enthalpy of formation is calculated from that of Cu(g) using $\Delta H_f^\circ(298.15 \text{ K}) = 46.0 \text{ kcal} \cdot \text{mol}^{-1}$ for Cu(g) obtained by 3rd law analysis of the mass spectrometric data of Ackerman *et al.*¹ Earlier studies of mass spectra and of the electronic band spectra yield values in reasonable agreement as shown below. The selected ΔH_f° corresponds to $D_0^\circ(0 \text{ K}) = 1.97 \text{ eV}$ compared with the linear Birge-Sponer extrapolation of 2.1 eV.

Source	Method	T/K	$\Delta H_f^\circ(298.15 \text{ K})$ 2nd law	$\Delta H_f^\circ(298.15 \text{ K})$ 3rd law	Drift $\text{cal K}^{-1} \cdot \text{mol}^{-1}$	$\Delta H_f^\circ(298.15 \text{ K})$ $\text{kcal} \cdot \text{mol}^{-1}$
1	Mass Spect.	1549–1709	47.8±2.6	45.99	—	116.0
2	Mass Spect.	1575–1720	50.3±3.7	46.76	−1.0±1.6	115.0
3	Mass Spect.	1440–1560	—	46.5	−2.1±2.3	115.5
4	Band Spectra	—	—	49.0	—	113.0

Heat Capacity and Entropy

Molecular constants, except for $\omega_e x_e$, were taken from the rotational analysis of bands of the B–X system given by Travis and Barrow.² The value for $\omega_e x_e$ was obtained from the earlier study of Kleman and Lindqvist⁴ who showed by means of the vibrational isotope effect that the emitter was Cu₂. The spectroscopic characters of the ground and excited states are uncertain, but Travis and Barrow indicate that the transition is probably $^1\Sigma_g^+ - ^1\Sigma_g^+$ for the B–X system. Vibrational and rotational constants were adjusted for 30.91% ^{63}Cu .

References

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T/K	C_p°	$S^\circ - [G^\circ - H(T)]/T$	$H^\circ - H(T)$	ΔH_f°	Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$	$\log K_r$
0	0	0	INFINITE	INFINITE	485.428	INFINITE
100	31.964	203.874	273.337	487.074	468.693	−244.820
200	35.442	227.321	245.038	486.456	450.478	−117.653
250	36.156	235.313	240.321	485.916	441.545	−92.256
298.15	36.585	241.721	241.721	485.344	433.051	−75.869
300	36.598	241.947	241.722	485.321	432.726	−75.344
350	36.893	247.612	242.168	484.686	424.010	−63.280
400	37.103	252.553	243.164	484.021	415.387	−54.244
450	37.261	256.933	244.455	483.329	406.849	−47.226
500	37.386	260.865	245.903	482.616	398.390	−41.619
600	37.576	267.699	248.983	481.124	381.683	−33.228
700	37.720	273.503	252.082	479.541	365.233	−27.254
800	37.840	278.548	255.082	477.872	349.016	−22.788
900	37.945	283.011	257.942	476.108	333.014	−19.328
1000	38.041	287.014	260.652	474.239	317.214	−16.370
1100	38.131	290.644	263.216	472.237	301.607	−14.322
1200	38.216	293.965	265.642	470.085	286.190	−12.458
1300	38.299	297.027	267.940	467.834	270.963	−10.887
1400	38.380	299.869	270.121	465.487	256.749	−9.579
1500	38.459	302.519	272.193	463.050	243.852	−8.492
1600	38.537	305.004	274.167	460.539	231.137	−7.546
1700	38.614	307.343	276.050	457.970	218.591	−6.716
1800	38.691	309.552	277.851	455.362	206.205	−5.984
1900	38.767	311.646	279.575	452.725	193.969	−5.333
2000	38.843	313.636	281.229	450.068	181.875	−4.750
2100	38.919	315.533	282.817	447.391	169.915	−4.226
2200	38.995	317.346	284.346	444.638	158.083	−3.753
2300	39.071	319.081	285.819	441.832	146.372	−3.324
2400	39.149	320.745	287.239	438.974	134.777	−2.933
2500	39.228	322.345	288.612	436.964	123.292	−2.576
2600	39.308	323.885	289.939	434.802	111.914	−2.248
2700	39.370	325.370	291.224	432.498	100.637	−1.947
2800	39.425	326.804	292.469	430.053	89.457	−1.669
2900	39.473	328.191	293.677	427.468	78.262	−1.408
3000	39.513	329.533	294.850	424.742	67.056	−1.149
3100	39.547	330.835	295.990	421.882	55.822	−0.883
3200	39.585	332.099	297.099	418.891	44.563	−0.616
3300	39.618	333.326	298.178	415.768	33.282	−0.353
3400	39.645	334.520	299.230	412.524	22.000	−0.092
3500	39.666	335.683	300.255	409.164	10.714	0.174
3600	39.683	336.816	301.255	405.698	−0.578	0.456
3700	39.695	337.922	302.231	402.138	−1.823	0.739
3800	39.701	339.001	303.184	398.484	−3.041	1.022
3900	39.702	340.055	304.116	394.738	−4.224	1.305
4000	39.700	341.087	305.027	390.902	−5.378	1.588
4100	39.694	342.096	305.919	386.976	−6.501	1.871
4200	39.683	343.085	306.793	382.959	−7.596	2.154
4300	39.668	344.053	307.648	378.852	−8.660	2.437
4400	39.649	344.999	308.486	374.664	−9.694	2.720
4500	39.625	345.936	309.308	370.396	−10.704	3.003
4600	39.596	346.851	310.114	366.056	−11.694	3.286
4700	39.562	347.751	310.905	361.646	−12.664	3.569
4800	39.523	348.635	311.682	357.164	−13.614	3.852
4900	39.479	349.505	312.445	352.610	−14.544	4.135
5000	39.430	350.361	313.195	348.000	−15.454	4.418
5100	39.376	351.203	313.932	343.334	−16.344	4.701
5200	39.317	352.033	314.657	338.612	−17.214	4.984
5300	39.253	352.851	315.370	333.834	−18.064	5.267
5400	39.185	353.657	316.071	329.000	−18.894	5.550
5500	39.113	354.452	316.762	324.114	−19.704	5.833
5600	39.037	355.236	317.442	319.174	−20.494	6.116
5700	38.957	356.009	318.112	314.184	−21.264	6.400
5800	38.872	356.773	318.772	309.144	−22.014	6.683
5900	38.782	357.527	319.422	304.054	−22.744	6.967
6000	38.687	358.272	320.064	298.914	−23.454	7.250

PREVIOUS September 1966 (1 atm)

CURRENT: September 1966 (1 bar)

Copper (Cu₂)Cu₂(g)

Copper Oxide (Cu₂O)

CRYSTAL

Copper Oxide (Cu₂O)

$S^{\circ}(298.15 \text{ K}) = 92.36 \pm 0.34 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T_{\text{fus}} = 1516.7 \text{ K}$
 $\Delta_f H^{\circ}(0 \text{ K}) = -168.95 \pm 2.1 \text{ kJ mol}^{-1}$
 $\Delta_f H^{\circ}(298.15 \text{ K}) = -170.71 \pm 2.1 \text{ kJ mol}^{-1}$
 $\Delta_{\text{ox}} H^{\circ} = 64.768 \pm 0.63 \text{ kJ mol}^{-1}$

Enthalpy of Formation

The enthalpy of formation of Cu₂O(cr) has been investigated calorimetrically (both oxidation and reduction reactions) and the oxidation reaction $2 \text{ Cu(cr)} + 1/2 \text{ O}_2(\text{g}) = \text{Cu}_2\text{O(cr)}$ has been studied extensively by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

Source	Method	Reaction*	T/K	Points	2nd law	$\Delta_f H^{\circ}(298.15 \text{ K})$, kcal mol ⁻¹	Drift	3rd law
1	Aq Calorim.	A	291	—	—	27.61	—	-40.70
2	Calorimetric	See Text	297.90	—	—	26.93	—	-40.83 ± 0.30
3	Aq emf	A	273-318	5	27.47 ± 0.04	—	0.4 ± 0.1	-41.39 ± 0.32
4	Aq emf	A	298-318	7	29.97 ± 0.38	—	-6.4 ± 1.3	-40.74
5*	q emf	A	288-308	3	29.54 ± 0.73	—	-4.3 ± 2.5	-40.30
6	Aq emf	B	1011-1156	5	-35.79 ± 0.86	—	-5.3 ± 0.8	-40.06
7	Equil Press	B	1073-1323	4	-42.29 ± 0.59	—	1.1 ± 0.5	-41.55
8	emf vs Fe/FeO	B	987	1	-60.17	—	-41.72	-40.96
9	Fused Salt emf	B	1100-1200	2	-41.10	—	-39.77 ± 2.03	-41.72
10	emf	B	973-1273	Eqn	-40.75	—	-40.75	-40.75
11	emf	B	892-1320	Eqn	-40.77	—	-40.77	-40.77
12	emf	B	1200-1420	Eqn	-40.30	—	-40.30	-40.30
13	Equil Press	B	1280-1450	Eqn	-36.82	—	-40.24	-40.24
14	Equil Press	B	973-1373	Eqn	-41.83	—	-41.01	-41.01
15	emf	B	845-1270	Eqn	-40.83	—	-40.88	-40.88
16	emf	B	976-1234	Eqn	-39.84	—	-40.59	-40.59
17	emf	B	1073-1273	Eqn	-41.07	—	-39.12	-40.59
18	emf	B	1013-1243	Eqn	-43.07	—	-43.86	-43.86
19	Equil Press	B	973-1273	Eqn	-42.62	—	-41.23	-41.23
20	emf	B	1173-1356	Eqn	-40.71	—	-40.90	-40.90
21	emf	B						

*Reactions (A) $2 \text{ Cu(cr)} + \text{H}_2\text{O(l)} = \text{Cu}_2\text{O(cr)} + \text{H}_2(\text{g})$ (B) $2 \text{ Cu(cr)} + 0.5 \text{ O}_2(\text{g}) = \text{Cu}_2\text{O(cr)}$

Thomsen¹ obtained $\Delta_f H^{\circ}(298.15 \text{ K})$ values of -40.18, -40.87, and -41.51 kcal mol⁻¹ from aqueous calorimetry using three different paths. He favored the first path which is recalculated by combination of the heats of reaction of Cu₂O + H₂SO₄, Fe + H₂SO₄, and Fe + CuSO₄(aq) to yield the heat of reduction of Cu₂O with H₂. Nunez *et al.*² measured the direct heat of reduction of Cu₂O by H₂ to conclude that the heats of formation of the copper oxides are influenced by material history, state of subdivision, and non stoichiometry. Mah *et al.*³ measured the direct heat of oxidation of copper by O₂, but they obtained a mixed product of Cu₂O and CuO and used $\Delta_f H^{\circ}(298.15 \text{ K}) = -33.63 \pm 0.05 \text{ kcal mol}^{-1}$ for the equilibrium reaction $\text{Cu}_2\text{O(cr)} + 1/2 \text{ O}_2(\text{g}) = 2 \text{ CuO(cr)}$ to resolve their results into $\Delta_f H^{\circ}(298.15 \text{ K})$ and $\Delta_f H^{\circ}(\text{CuO, cr, } 298.15 \text{ K})$. The overall average from our 3rd law analyses is -40.82 kcal mol⁻¹, without the outlier¹⁰ is the average is 40.81, the average of the six data sets with an absolute drift less than 1 is -40.77. We adopt $\Delta_f H^{\circ}(\text{Cu}_2\text{O, cr, } 298.15 \text{ K}) = -40.8 \pm 0.5 \text{ kcal mol}^{-1}$.

Heat Capacity and Entropy

The heat capacities are smoothed values adopted from a consideration of the work of Gregor²² (2.8-21 K), Hu and Johnston²³ (15-300 K) and Mah *et al.*² (52-296 K, 406-1464 K). The data of Mah *et al.*² are favored over that of Hu and Johnston²³ above 120 K. Adjustment is made to the IPTS 68 temperature scale²⁴.

The entropy is based on a T° extrapolation to obtain $S^{\circ}(2.8 \text{ K}) = 0.0015 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

- ¹J. Thomsen, "Thermochemische Untersuchungen," Vol. III, Barth, Leipzig, (1883).
²A. D. Mah, L. B. Pankratz, W. W. Weller and E. G. King, U. S. Bur. Mines RI 7026, (1967).

Continued on page 1027

Copper Oxide (Cu₂O)

PREVIOUS: June 1966

CURRENT: December 1977

Cu₂O₁(cr)

Enthalpy Reference Temperature = T, = 298.15 K				Standard State Pressure = p° = 0.1 MPa			
T/K	C _p ^a	S°	[C _p - H°(T)]/T	H° - H°(T)	Δ _f H°	Δ _f G°	log K _f
0	0	0	INFINITE	-12.600	-168.952	-168.952	INFINITE
100	39.499	37.092	141.510	-10.442	-169.584	-162.621	84.944
200	53.619	69.143	97.826	-5.737	-170.360	-155.348	40.573
298.15	62.543	92.360	92.360	0	-170.707	-147.886	25.909
300	62.664	92.747	92.361	0.116	-170.709	-147.745	25.725
400	67.688	111.531	94.888	6.657	-170.641	-140.092	18.294
500	70.922	127.000	99.809	13.596	-170.363	-137.484	13.840
600	73.448	140.161	105.465	20.818	-169.961	-124.944	10.877
700	75.645	151.651	111.259	28.274	-169.479	-117.478	8.766
800	77.666	161.886	116.959	35.941	-168.929	-110.087	7.188
900	79.493	171.141	122.473	43.801	-168.325	-102.767	5.964
1000	81.245	179.606	127.769	51.837	-167.688	-95.517	4.989
1100	83.385	187.443	132.842	60.061	-167.029	-88.331	4.194
1200	86.110	194.812	137.702	68.532	-166.322	-81.208	3.535
1300	89.173	201.824	142.367	77.294	-165.608	-74.144	2.979
1400	92.489	208.552	146.855	86.375	-164.855	-67.165	2.474
1500	95.987	215.052	151.186	95.798	-164.075	-60.321	2.000
1516.700	96.587	216.118	151.895	97.406	-163.932	-57.438	2.000
1600	99.631	221.362	155.376	105.578	-163.755	-48.635	1.588
1700	103.380	227.514	159.439	115.728	-163.529	-39.928	1.227
1800	107.212	233.532	163.389	126.257	-163.257	-31.335	0.909
1900	111.115	239.433	167.236	137.173	-162.940	-22.868	0.629
2000	115.068	245.232	170.992	148.481	-162.581	-14.542	0.380

--- CRYSTAL ---> LIQUID ---> LIQUID

Copper Oxide (Cu₂O)

$$S^{\circ}(298.15 \text{ K}) = [129.957] \text{ J K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{fus}} = 1516.7 \text{ K}$$

Enthalpy of Formation

$\Delta_f H^{\circ}(\text{Cu}_2\text{O}, 1, 298.15 \text{ K})$ is calculated from that of the crystal by adding $\Delta_{\text{fus}} H^{\circ}$ and the difference in enthalpy, $H^{\circ}(1516.7 \text{ K}) - H^{\circ}(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is taken from the enthalpy measurements of Mah *et al.*¹ (1521–1600 K) and is assumed constant at 23.88 cal K⁻¹·mol⁻¹ from 1000 to 2000 K. A glass transition is assumed at 1000 K below which the heat capacity is that of the crystal.

The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting point, 1515 K, was determined by drop calorimetry by Mah *et al.*¹ Correcting to the IPTS-68 temperature scale,² we adopt $T_{\text{fus}} = 1516.7 \text{ K}$.

$\Delta_{\text{fus}} H^{\circ} = 15.48 \pm 0.15 \text{ kcal} \cdot \text{mol}^{-1}$ is based on our smoothing through the pre-melt region of the enthalpy measurements of Mah *et al.*¹

References

- ¹A. D. Mah, L. B. Pankratz, W. W. Weller and E. G. King, U. S. Bur. Mines RI 7026, (1967).
- ²The International Practical Temperature Scale of 1968, *Metologia* 5, 35 (1969); T. B. Douglas, *J. Res. Nat. Bur. Stand.* 73A, 451 (1969).

$$M_r = 143.0914$$

Copper Oxide (Cu₂O)

LIQUID

Cu₂O(l)

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$					Standard State Pressure = $p^{\circ} = 0.1 \text{ MPa}$				
T/K	C_p°	S°	$-(G^{\circ} - H^{\circ}(T))/T$	$H^{\circ} - H^{\circ}(T_r)$	$\Delta_f H^{\circ}$	$\Delta_f G^{\circ}$	$\log K_r$		
0									
100									
200									
298.15	62.542	129.957	129.957	0.	-111.995	-100.384	17.587		
300	62.664	130.345	129.959	0.116	-111.997	-100.312	17.466		
400	67.688	149.128	132.486	6.657	-111.929	-96.419	12.591		
500	70.922	164.598	137.407	13.596	-111.651	-92.570	9.671		
600	73.448	177.758	143.062	20.818	-111.249	-88.701	7.730		
700	75.645	189.249	148.857	28.274	-110.767	-85.085	6.549		
800	77.666	199.483	154.557	35.941	-110.217	-81.432	5.318		
900	79.493	208.739	160.071	43.801	-109.613	-77.893	4.521		
1000	81.245	217.203	165.367	51.837	-108.976	-74.402	3.866		
1000.000	81.245	217.203	165.367	51.837					
1000.000	99.914	217.203	165.367	51.837					
1100	99.914	226.776	170.519	61.828	-106.550	-71.064	3.375		
1200	99.914	235.420	175.570	71.819	-104.523	-67.938	2.957		
1300	99.914	243.417	180.486	81.811	-102.580	-64.987	2.611		
1400	99.914	250.872	185.249	91.802	-100.726	-61.360	2.289		
1500	99.914	257.715	189.853	101.794	-98.924	-56.725	1.975		
1516.700		258.821	190.606	103.462					
1600	99.914	264.163	194.298	111.785	--- CRYSTAL ---> LIQUID ---				
1700	99.914	270.220	198.587	121.776	-123.856	-52.197	1.704		
1800	99.914	275.931	202.727	131.768	-122.259	-47.768	1.468		
1900	99.914	281.333	206.723	141.759	-120.694	-43.431	1.260		
2000	99.914	286.458	210.583	151.751	-119.142	-39.181	1.077		
					-117.600	-35.013	0.914		

PREVIOUS: June 1966

CURRENT: December 1977

Copper Oxide (Cu₂O)Cu₂O(l)

CRYSTAL-LIQUID

0 to 1516.7 K crystal
above 1516.7 K liquid

Refer to the individual tables for details.

 $M_r = 143.0914$ Copper Oxide (Cu_2O) $\text{Cu}_2\text{O}_1(\text{cr,l})$

Enthalpy Reference Temperature = $T_r = 298.15$ K		Standard State Pressure = $p^\circ = 0.1$ MPa			
T/K	C_p° J·K ⁻¹ ·mol ⁻¹	$S^\circ - [G^\circ - H^\circ(T_r)]/T_r$ J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹		
			$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
0	0.	0.	-12.600	-168.952	-168.952
100	39.499	37.092	-10.442	-169.584	-162.621
200	53.619	69.143	-5.737	-170.360	-155.348
298.15	62.543	92.360	0.	-170.707	-147.886
300	62.664	92.747	0.116	-170.709	-147.745
400	67.688	111.531	6.637	-170.641	-140.092
500	70.922	127.000	13.596	-170.565	-132.484
600	73.448	140.161	20.818	-169.961	-124.944
700	75.645	151.651	28.274	-169.479	-117.478
800	77.666	161.886	35.941	-168.929	-110.087
900	79.493	171.141	43.801	-168.325	-102.767
1000	81.245	179.606	51.837	-167.688	-95.517
1100	83.385	187.443	60.061	-167.029	-88.331
1200	86.110	194.812	68.532	-166.322	-81.208
1300	89.173	201.824	77.294	-165.608	-74.144
1400	92.489	208.552	86.375	-164.165	-66.321
1500	95.987	215.052	95.798	-160.132	-57.438
1516.700	96.587	216.118	97.406	CRYSTAL \leftrightarrow LIQUID TRANSITION	
1516.700	99.914	258.821	162.174		
1600	99.914	264.163	170.497	-123.836	-52.197
1700	99.914	270.220	180.488	-122.259	-47.768
1800	99.914	275.931	190.480	-120.694	-43.431
1900	99.914	281.333	200.471	-119.142	-39.181
2000	99.914	286.458	210.463	-117.600	-35.013

PREVIOUS:

CURRENT: December 1977

Copper Oxide (Cu_2O) $\text{Cu}_2\text{O}_1(\text{cr,l})$

Copper Oxide Sulfate (CuO·CuSO₄)

CRYSTAL

$$M_r = 239.1490$$

$$S^\circ(298.15\text{ K}) = [157.318 \pm 8.4] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_f H^\circ(298.15\text{ K}) = -927.593 \pm 1.3 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(0\text{ K}) = \text{Unknown}$$

Enthalpy of Formation

The equilibrium pressures for the following reactions: (A) CuO·CuSO₄(cr) = 2 CuO(cr) + SO₂(g) and SO₂(g) = SO₃(g) + 0.5 O₂(g) and (B) CuO·CuSO₄(cr) + Cu₂O(cr) = 4 CuO(cr) + SO₂(g), were determined by Reinders¹ and Ingraham.² Using the reported vapor pressures, the corresponding enthalpy changes were evaluated by both the 2nd and 3rd law methods. The results obtained are presented as follows:

Reference	Reaction	T/K	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹	2nd law	3rd law	Drift	$\Delta_f H^\circ(298.15\text{ K})$, kcal·mol ⁻¹
1	A*	1013–1093	53.03 ± 2.53	52.43	52.43	-0.7 ± 2.4	-221.5
1	B	917–1027	41.72 ± 1.42	42.43	42.43	0.5 ± 1.4	-221.7
2	A*	969–1138	50.97 ± 0.16	52.57	52.57	1.5 ± 0.2	-221.7

*Partial pressures were calculated from JANAF values for the SO₃ – SO₂ equilibrium.
The value of $\Delta_f H^\circ(\text{CuO} \cdot \text{CuSO}_4, \text{cr}, 298.15\text{ K})$ adopted is $-221.7 \pm 0.3 \text{ kcal mol}^{-1}$.

Heat Capacity and Entropy

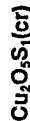
The heat capacities are calculated as the sum of those for CuO(cr) and CuSO₄(cr). The value of $S^\circ(298.15\text{ K})$ is estimated by comparison with those for CuO(cr) and CuSO₄(cr) and adjusted so that, using the derived free energy functions, the 2nd and 3rd law values for $\Delta_f H^\circ(298.15\text{ K})$ agree reasonably.

Decomposition Data

$T_{\text{dec}} = 1138\text{ K}$ is the temperature at which the total pressure of the gaseous decomposition products of reaction (A) equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for CuO·CuSO₄(cr), determined by Ingraham.²

References

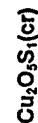
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Copper Oxide Sulfate (CuO·CuSO₄)

Enthalpy Reference Temperature = T, = 298.15 K					Standard State Pressure = p° = 0.1 MPa		
T/K	C _p ^a	S°	-[G° - H°(T)]/T	H° - H°(T)	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K _r
0							
100							
200							
298.15	141.043	157.318	157.318	0.	-927.593	-792.253	138.799
300	141.419	158.192	157.321	0.261	-927.600	-791.413	137.797
400	162.339	201.891	163.137	15.501	-929.372	-745.953	97.411
500	176.983	239.760	174.761	32.499	-929.081	-700.122	73.141
600	187.870	273.029	188.423	50.763	-927.541	-654.457	56.976
700	195.811	302.603	202.662	69.959	-925.177	-609.121	45.453
800	202.129	329.172	216.843	89.863	-922.273	-564.163	36.836
900	207.526	353.295	230.685	110.349	-917.111	-518.512	30.094
1000	212.547	375.424	244.067	131.356	-907.283	-468.369	24.465
1100	217.150	395.897	256.951	152.841	-892.253	-418.719	19.883
1200	221.752	414.990	269.334	174.787	-875.056	-369.536	16.085
1300	226.313	432.923	281.235	197.194	-851.765	-320.790	12.889
1400	230.329	449.842	297.680	220.077	-827.716	-271.639	10.135
1500	234.304	465.869	303.696	243.259	-807.089	-221.757	7.722

PREVIOUS:

CURRENT: June 1966

Copper Oxide Sulfate (CuO·CuSO₄)

Continued from Page 1023

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