Molybdenum (Mo)

REFERENCE STATE

A_r = 95.94  Molybdenum (Mo)  Mo_1(ref)

<table>
<thead>
<tr>
<th>T/K</th>
<th>C_T</th>
<th>S^* - (ln(T/μ))/T</th>
<th>H^*/H(298.15K)</th>
<th>ΔH^*</th>
<th>ΔC^*</th>
<th>log K_r</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0. INFINITE</td>
<td>-4.583</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>100</td>
<td>13.493</td>
<td>7276</td>
<td>47.961</td>
<td>-4.994</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>200</td>
<td>21.507</td>
<td>19.478</td>
<td>20.733</td>
<td>-2.251</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>298.15</td>
<td>23.933</td>
<td>28.602</td>
<td>28.605</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>300</td>
<td>23.958</td>
<td>28.723</td>
<td>28.606</td>
<td>0.044</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>400</td>
<td>25.080</td>
<td>33.810</td>
<td>29.565</td>
<td>2.500</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>500</td>
<td>25.830</td>
<td>41.494</td>
<td>31.397</td>
<td>5.049</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>600</td>
<td>26.460</td>
<td>46.763</td>
<td>33.487</td>
<td>7.665</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>700</td>
<td>26.980</td>
<td>50.382</td>
<td>35.413</td>
<td>10.338</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>800</td>
<td>27.440</td>
<td>54.015</td>
<td>37.461</td>
<td>12.059</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>900</td>
<td>27.890</td>
<td>57.272</td>
<td>39.689</td>
<td>13.825</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1000</td>
<td>28.370</td>
<td>60.323</td>
<td>41.977</td>
<td>15.557</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1100</td>
<td>28.900</td>
<td>62.963</td>
<td>43.417</td>
<td>17.291</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1200</td>
<td>29.490</td>
<td>65.502</td>
<td>45.153</td>
<td>19.006</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1300</td>
<td>30.140</td>
<td>67.888</td>
<td>46.811</td>
<td>20.709</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1400</td>
<td>30.860</td>
<td>70.148</td>
<td>48.399</td>
<td>22.402</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1500</td>
<td>31.600</td>
<td>72.304</td>
<td>49.930</td>
<td>24.090</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1600</td>
<td>32.500</td>
<td>74.373</td>
<td>51.384</td>
<td>25.778</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1700</td>
<td>33.430</td>
<td>76.371</td>
<td>52.796</td>
<td>27.460</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1800</td>
<td>34.420</td>
<td>78.309</td>
<td>54.160</td>
<td>29.139</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>1900</td>
<td>35.490</td>
<td>80.198</td>
<td>55.481</td>
<td>29.702</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2000</td>
<td>36.650</td>
<td>82.045</td>
<td>56.763</td>
<td>30.287</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2100</td>
<td>37.900</td>
<td>83.866</td>
<td>58.010</td>
<td>30.847</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2200</td>
<td>39.240</td>
<td>85.659</td>
<td>59.224</td>
<td>31.397</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2300</td>
<td>40.670</td>
<td>87.435</td>
<td>60.414</td>
<td>31.937</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2400</td>
<td>42.210</td>
<td>89.199</td>
<td>61.577</td>
<td>32.478</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2500</td>
<td>43.850</td>
<td>90.954</td>
<td>62.717</td>
<td>33.019</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2600</td>
<td>45.590</td>
<td>92.713</td>
<td>63.837</td>
<td>33.559</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2700</td>
<td>48.370</td>
<td>94.490</td>
<td>64.959</td>
<td>34.099</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>2800</td>
<td>51.570</td>
<td>96.304</td>
<td>66.027</td>
<td>34.640</td>
<td>0.</td>
<td>0.</td>
</tr>
</tbody>
</table>

NIST-JANAF THERMOCHEMICAL TABLES

Molybdenum (Mo)  Mo_1(ref)

PREVIOUS: March 1978 (1 atm)  CURRENT: March 1978 (1 bar)
Molybdenum (Mo)  

**CRYSTAL**  

$A_i = 95.54$  

$\Delta H^\circ(298.15 \, K) = 28.605 \pm 0.050 \, \text{kJ} \cdot \text{mol}^{-1}$  

$T_{\text{m}} = 2896 \pm 8 \, \text{K}$  

**Enthalpy of Formation**  

Zero by definition.  

**Heat Capacity and Entropy**  

The low temperature heat capacities of Mo(cr) have been measured by Clusius and Franzonis (1959) between 16 and 256 K (63 measured $C_p$ points). The reported $C_p$ values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure also includes the smoothed $C_p$ values (275–335 K) reported in the critical evaluation by Dittmars et al. (1958) as to provide smoothly varying heat capacity values in the range 256–275 K. The data of Simon and Zeidler, (15–238 K), are as much as 2.5% high below 78 K and as much as 1% low above 78 K. 

Below 20 K several investigators (1) have determined the heat capacity. Heiniger et al. (1964) have summarized and critically reviewed this work as well as other studies. These sources give $S(20 \, K)$ values in the range 0.021–0.025 cal·K$^{-1}$·mol$^{-1}$. Adopting $S(20 \, K) = 0.024$ cal·K$^{-1}$·mol$^{-1}$ and combining this with our analysis of the Clusius and Franzonis work, we calculate $S(298.15 \, K) = 6.836 \pm 0.012$ cal·K$^{-1}$·mol$^{-1}$. This result agrees with the review of the heat capacity data ($T < 298.15 \, K$) by Reilly and Furukawa (1964) for Brewer. 

The high temperature heat capacity values, 273–2980 K, are those selected by Dittmars et al. (1958) This study reports three recent NBS heat capacity/enthalpy studies covering the 270–2800 K NBS Standard Reference Material No. 781. In addition, the report contains a bibliography of publications on the high temperature enthalpy and heat capacity of crystalline molybdenum. A graphical comparison of the NBS results with those of all the principal investigators and critical evaluation is also given in the publication. These results are linearly extrapolated from 2800 K to 3300 K. The high temperature heat capacity values adopted by Brewer (1964) based on IPTS-48, are within 0.1% of the NBS results between 298 and 900 K and are 0.2 to 0.3% higher between 1000 and 1400 K. Between 1500 and 1900 K, the difference is less than 0.1%. From 2000 to 2300 K, the values are 0.2 to 0.3% lower and are 0.1% to 0.2% high between 2400 to 2700 K. The value at 2800 K is 0.5% lower than our adopted value. At 2800 K, the entropy difference is 0.004 cal·K$^{-1}$·mol$^{-1}$ with the JANAF value being smaller. 

**Fusion Data**  

Refer to the liquid table for details. 

**Sublimation Data**  

Eight sublimation studies are discussed on the ideal gas table. 

**References**  

### Molybdenum (Mo)

<table>
<thead>
<tr>
<th>$\Delta H_f^o$ (298.15 K) [kJ mol$^{-1}$]</th>
<th>$\Delta_{m}H^o$ (moi) [kJ mol$^{-1}$]</th>
<th>$\Delta_{m}G^o$ (moi) [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>147.56</td>
<td>147.56</td>
<td>147.56</td>
</tr>
</tbody>
</table>

### Liquid

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta H_f^o$ (298.15 K) [kJ mol$^{-1}$]</th>
<th>$\Delta_{m}H^o$ (moi) [kJ mol$^{-1}$]</th>
<th>$\Delta_{m}G^o$ (moi) [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>147.56</td>
<td>147.56</td>
<td>147.56</td>
</tr>
<tr>
<td>300</td>
<td>147.56</td>
<td>147.56</td>
<td>147.56</td>
</tr>
<tr>
<td>305</td>
<td>147.56</td>
<td>147.56</td>
<td>147.56</td>
</tr>
</tbody>
</table>

### Fusion Data

The adopted melting point, $T_m = 2896 \pm 8$ K, is derived from the recent experimental study and critical evaluation of earlier data by Kenisari et al.

Berezin et al. have measured the enthalpy of fusion of molybdenum by levitation calorimetry in the range 1962-2659 K and 2890-2925 K, respectively. They reported $\Delta_{m}H^o = 8.741 \pm 0.314 \text{ kcal mol}^{-1}$ at an assumed melting temperature of 2900 K. Correcting these results to $T_m = 2896$ K yields $8.693 \pm 0.314 \text{ kcal mol}^{-1}$. Berezin et al. using a pulse-heating technique, reported enthalpy measurements (1978-4500 K) which gave $\Delta_{m}H^o = 8.553 \text{ kcal mol}^{-1}$ at a melting point of 2923 K.

Treverton and Margreave also have used levitation calorimetry to measure the liquid phase enthalpy of molybdenum in the range 2693-3115 K. Using the enthalpy value for the liquid at the melting point as determined by Treverton and Margreave and the enthalpy value of the crystal at the melting point as determined by our adopted functions, we calculate $\Delta_{m}H^o = 7.264 \text{ kcal mol}^{-1}$. Lebedev et al. reported $\Delta_{m}H^o = 9.864 \text{ kcal mol}^{-1}$ (exploding wire technique) while Kostikov et al. found $\Delta_{m}H^o = 6.095 \text{ kcal mol}^{-1}$ (drop technique).

We adopt $\Delta_{m}H^o = 8.6 \pm 1.3 \text{ kcal mol}^{-1}$, which corresponds to $\Delta_{m}S^o = 2.97 \text{ cal K}^{-1} \text{ mol}^{-1}$. This $\Delta_{m}S^o$ appears high for a metal with a bcc (A2) structure; however, this value is supported by the studies of Berezin et al. and Shaker et al. Brewer selected a value of $\Delta_{m}H^o = 8.54 \pm 0.3 \text{ kcal mol}^{-1}$ (ITPS-48).

### Vaporization Data

The boiling point and enthalpy of vaporization are calculated from the adopted functions and enthalphy of sublimation in order to maintain proper thermodynamic consistency.

### References

9. L. Bjerke, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
### Crystal-Liquid

$A_i = 95.94$  Molybdenum (Mo)

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$C_j^*$</th>
<th>$S_j^*$</th>
<th>$-\Delta G_j^*(H^0_T)/J$</th>
<th>$H^0_r-H^0(T_0)$</th>
<th>$\Delta H^0$</th>
<th>$\Delta G^0$</th>
<th>$\log K_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>INFINITY</td>
<td>-4.585</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>3.345</td>
<td>0.006</td>
<td>7.961</td>
<td>28.95</td>
<td>-1.133</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>250</td>
<td>25.006</td>
<td>28.753</td>
<td>28.753</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>5.000</td>
<td>2.450</td>
<td>2.450</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>350</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>450</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>550</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>650</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>750</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>850</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>950</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1050</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1100</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1150</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1200</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1250</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1300</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1350</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1400</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1450</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1500</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1550</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1600</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1650</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1700</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1750</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1800</td>
<td>2.500</td>
<td>3.250</td>
<td>3.250</td>
<td>2.949</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

PREVIOUS: CURRENT: March 1978
## Molybdenum (Mo)

### Ideal Gas

<table>
<thead>
<tr>
<th>Data Points</th>
<th>T/K</th>
<th>( \Delta H^0(298.15 \text{ K}) ), kcal mol(^{-1} )</th>
<th>Drift cal-K mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>eqn</td>
<td>1201–2396</td>
<td>159.8 ± 0.7</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>2068–2500</td>
<td>162.2 ± 2.6</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>2144–2537</td>
<td>153.8 ± 0.9</td>
</tr>
<tr>
<td>4</td>
<td>eqn</td>
<td>1361–2297</td>
<td>148.8 ± 0.7</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>2089–2493</td>
<td>156.8 ± 0.6</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>2293–2673</td>
<td>152.4 ± 1.2</td>
</tr>
</tbody>
</table>

A mass spectrometric study of the enthalpy of sublimation of molybdenum\(^2\) yielded, \( \Delta H^0(2500 \text{ K}) = 144.1 ± 2.2 \text{ kcal mol}^{-1} \), correcting to 298.15 K, we calculate \( \Delta H^0(298.15 \text{ K}) = 145.9 ± 2.3 \text{ kcal mol}^{-1} \). We adopt \( \Delta H^0(298.15 \text{ K}) = 157.3 ± 0.9 \text{ kcal mol}^{-1} \) from a consideration of five studies.\(^3\) Brewer\(^4\) has adopted a value of 0.2 kcal mol\(^{-1}\) less positive, however his vapor pressure analysis is based on the 1948 temperature scale.

### Heat Capacity and Density

The electronic energy levels are given in the compilations by Moore.\(^5\) Although we have only listed the ground state, first excited state, highest observed excited state, and the ionization limit for Mo(g), all levels listed by Moore\(^6\) as well as estimated levels, are used in our calculations. The observed levels are too numerous to list completely. An examination of the estimates for missing levels suggests they all lie above 20000 cm\(^{-1}\). Our calculations indicate that for Mo(g) the thermochromic functions are independent of the estimated missing levels (for \( n = 5, 6, 7 \)), the cut-off procedure, and the inclusion of \( n = 6, 7 \) levels up to 5000 K. The Gibbs energy function is essentially unaffected even above 4000 K. The reported uncertainty in \( \Delta H^0(298.15 \text{ K}) \) is due to uncertainties in the relative atomic gas and fundamental constants. Extension of these estimates above 6000 K may require consideration of the higher excited states and utilization of proper filter and cut-off procedures.\(^7\) In fact, the inclusion of some higher states (\( n = 5, 6, 7 \)) and consideration of various cut-off procedures leads to calculated differences in the Gibbs energy functions of roughly 0.1 kcal mol\(^{-1}\) or greater at temperatures in excess of 6000 K. The thermal functions adopted here are the same as those of Brewer.\(^8\)

### References

11. **B. Brewer, Materials and Molar Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.**

---

### NIST-JANAF Thermochemical Tables

**Molybdenum (Mo)**

<table>
<thead>
<tr>
<th>T/K</th>
<th>( C_p^o ) ( ^o \text{J} \text{mol}^{-1} \text{K}^{-1} )</th>
<th>( \Delta H^o(298.15 \text{ K}) ), kcal mol(^{-1} )</th>
<th>( \Delta S^o(298.15 \text{ K}) ), e.u.</th>
<th>( \Delta G^o(298.15 \text{ K}) ), kcal mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>INFINITE</td>
<td>0</td>
<td>0</td>
<td>INFINITE</td>
</tr>
<tr>
<td>100</td>
<td>20,786 159.243</td>
<td>200,431</td>
<td>0</td>
<td>244,431</td>
</tr>
<tr>
<td>200</td>
<td>20,786 175.631</td>
<td>200,431</td>
<td>0</td>
<td>244,431</td>
</tr>
<tr>
<td>300</td>
<td>20,786 189.343</td>
<td>200,431</td>
<td>0</td>
<td>244,431</td>
</tr>
</tbody>
</table>
Molybdenum, Ion (Mo⁺)

**IDEAL GAS**

$M = 95.93945$

$IP(Mo⁺, g) = 130000 ± 500 \text{ cm}^{-1}$

$S^*(298.15 \text{ K}) = 180.669 ± 0.05 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H^\circ(0 \text{ K}) = 1342.35 ± 4.0 \text{ kJ mol}^{-1}$

$\Delta H^\circ(298.15 \text{ K}) = [1350] 159 \text{ kJ mol}^{-1}$

<table>
<thead>
<tr>
<th>Electronic Levels and Quantum Weights</th>
<th>$\epsilon_u \text{ cm}^{-1}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S_2$</td>
<td>0.00</td>
<td>6</td>
</tr>
<tr>
<td>$^3S_2$</td>
<td>1783.36</td>
<td>2</td>
</tr>
<tr>
<td>$^1D_2$</td>
<td>12034.06</td>
<td>6</td>
</tr>
<tr>
<td>$^3D_2$</td>
<td>12442.28</td>
<td>3</td>
</tr>
<tr>
<td>$^1D_2$</td>
<td>12000.33</td>
<td>8</td>
</tr>
<tr>
<td>$^3D_2$</td>
<td>13460.70</td>
<td>10</td>
</tr>
</tbody>
</table>

**Enthalpy of Formation**

$\Delta H^\circ(\text{Mo}^+, \text{ g, 0 \text{ K}})$ is calculated from $\Delta H^\circ(\text{Mo}^+, \text{ g, 0 \text{ K}})$ using the spectroscopic value of IP(\text{Mo}) = 57260 ± 50 cm$^{-1}$ (684.982 ± 0.60 kJ mol$^{-1}$) from Moore. The ionization limit is converted from cm$^{-1}$ to kJ mol$^{-1}$ using the factor, $1 \text{ cm}^{-1} = 0.0196266 \text{ kJ mol}^{-1}$, which is derived from the 1973 CODATA fundamental constants$^3$ Rosensweig et al. and Levin and Lias$^2$ have summarized additional ionization and appearance potential data.

$\Delta H^\circ(\text{Mo}^+, \text{ g, 298.15 \text{ K}})$ is calculated from $\Delta H^\circ(\text{Mo}^+, \text{ g, 0 \text{ K}})$ by using IP(\text{Mo}) with JANAF enthalpies, $H^0(\text{g})$ and $H^0(\text{298.15 K})$, for Mo(g), MoO(g), and $\epsilon(\text{g})$. $\Delta H^\circ(\text{Mo}^+, \text{ g, 298.15 \text{ K}})$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosensweig et al.$^4$ $\Delta H^\circ(\text{Mo}^+, \text{ g, 298.15 \text{ K}})$ should be changed by $-6.197 \text{ kJ mol}^{-1}$ if it is to be used in the ion convection that excludes the enthalpy of the electron.

**Heat Capacity and Entropy**

The information on electronic energy levels and quantum weights, given by Moor,$^2$ is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for Mo(g), all levels listed by Moor, as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Mo(g), the thermodynamic functions are independent of the estimated missing levels (for $\Delta = 4, 5$), the cut-off procedure, and the inclusion of $n = 5$ levels up to 4000 cm$^{-1}$, the Gibbs energy function showing variations of 0.4 kJ mol$^{-1}$ at this temperature. The reported uncertainty in $S^*(298.15 \text{ K})$ 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 higher excited states (e.g., 7s), and use of different cut-off and cut-off procedures.$^1$

![Image](image_url)

**References**

1. JANAF Thermochemical Tables: Mo(g), 3-31-78; $\epsilon(\text{g})$, 3-31-82.
**Molybdenum, Ion (Mo⁺)**

**IDEAL GAS**

\[ M = 95.94055 \text{ Molybdenum, Ion (Mo⁺)} \]

| \( \Delta H^\circ (0 \text{ K}) \) | 585.390 ± 1.5 kJ mol\(^{-1} \) |
| \( \Delta H^\circ (298.15 \text{ K}) \) | 350.803 \text{ kJ mol}\(^{-1} \) |

<table>
<thead>
<tr>
<th>Electronic Level and Quantum State</th>
<th>( e_\text{s} ) cm(^{-1} )</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{S} \text{D}_{2} )</td>
<td>0.0</td>
<td>6</td>
</tr>
</tbody>
</table>

**Enthalpy of Formation**

\[ \Delta H^\circ (\text{Mo}^+, 0 \text{ K}) = \text{calculated from } \Delta H^\circ (\text{Mo}^+, 0 \text{ K}) \text{ using the adopted electron affinity of } \text{EA(\text{Mo})} = 0.746 \pm 0.010 \text{ eV} \]  

This value, recommended by Hotop and Lineberger,\(^4\) is based on a laser photoelectron emission spectrometry study. Additional information on Mo\(^+\) may be obtained in the critical discussions of Hotop and Lineberger.\(^5\) Rosenstock et al.\(^6\) and Massey.\(^7\)

\[ \Delta H^\circ (\text{Mo}^+, 298.15 \text{ K}) = \text{obtained from } \Delta H^\circ (\text{Mo}^+, 0 \text{ K}) \text{ by using EA(\text{Mo}) with JANAF}\(^8\) enthalpies, } H^\circ (0 \text{ K}) = H^\circ (298.15 \text{ K}) \text{, or } \text{Mo}^+, \text{Mo}^+, \text{and } e^- \text{ (ref } \Delta H^\circ (\text{Mo}^+ \rightarrow \text{Mo}^+ + e^-, 298.15 \text{ K}) \text{ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.} \text{ ΔH}(298.15 \text{ K}) \text{ should be changed by +6.197 kJ mol}^{-1} \text{ 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 Mo\(^+\) is given by Hotop and Lineberger\(^4\) and Rosenstock et al.\(^6\) Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

**References**

1. JANAF Thermochemical Tables: Mo\(^+\), 3–13–78; e\(^-\) (ref), 3–13–82.


PREVIOUS March 1978 (1 am) CURRENT March 1994 (1 bar)
Molybdenum Oxide (MoO)  

**Ideal Gas** 

\[ \Delta H_f^\circ(0 \text{ K}) = 310.25 \pm 33.5 \text{ kJ mol}^{-1} \]

\[ \Delta H_f^\circ(298.15 \text{ K}) = 310.96 \pm 33.5 \text{ kJ mol}^{-1} \]

**Electronic Levels and Quantum Weights**

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \alpha_n )</th>
<th>( \beta_n )</th>
<th>( \gamma_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.99 cm(^{-1})</td>
<td>(9900 cm(^{-1}))</td>
<td>0.2044 ( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>1</td>
<td>1.74 ( \text{cm}^{-1} )</td>
<td>0.0044 ( \text{cm}^{-1} )</td>
<td>0.2044 ( \text{cm}^{-1} )</td>
</tr>
</tbody>
</table>

**Enthalpy of Formation**

The enthalpy of formation of MoO\(_4\) is taken from the critical analysis of the MoO system by Brewer.\(^1\) The adopted value is \( \Delta H_f^\circ(298.15 \text{ K}) = 74.32 \pm 8 \text{ kCal mol}^{-1} \). All the current JANAF Thermochromical Tables for molybdenum-oxygen species are based on the internally consistent values of Brewer.\(^1\)

Choudary et al.\(^2\) have reviewed earlier data and evaluations of \( \Delta H_f^\circ \) for MoO\(_4\). They have also presented new data between 1462 and 1958 K. For the reaction 2 MoO\(_3\)(g) = MoO\(_4\)(g) + MoO\(_2\)(g), the 3rd law values are mostly in the range 2.44 to 4.6 kCal mol\(^{-1}\) compared to 2nd law values of 7.8 kCal mol\(^{-1}\) or more negative. \( \Delta H_f^\circ(2200 \text{ K}) = 112 \text{ kCal mol}^{-1} \) was selected by Brewer for the reaction as written.

**Heat Capacity and Entropy**

The ground state configuration is assumed to be similar to that for gaseous WO\(_3\), Swaminathan and Krishnamurthy\(^4\) observed ten band systems which they attributed to molybdenum oxide with lower state values of \( \alpha = 950 \pm 10 \text{ cm}^{-1} \). Ions and Squibb\(^5\) also observed a band with a peak at 969 cm\(^{-1}\) in the vapor above MoO\(_3\)(cr). It is surprising that the observed vibrational frequency of MoO\(_3\) is lower than 1055 cm\(^{-1}\) observed for WO\(_3\). The latter comes not only from electronic spectra of the gas but also from infrared absorption in the matrix isolation, the former comes from internal rotations of a symmetric assignments of electronic spectra presumably arising from MoO\(_3\). It is possible that the observed states could be low lying excited states. We tentatively assume the fundamental vibrational frequency to be 1000 \pm 20 \text{ cm}^{-1}. The anharmonicity correction \( \alpha \) is estimated from the relation \( \alpha = 0.014 \text{ given by Barrow and Caunt}\(^6\). The constant (0.014) is assumed to be the same for both WO\(_3\) and MoO\(_3\). The value of \( \alpha \) is calculated from the Morse potential function. Schröder\(^2\) gave a relationship between bond order and Mo-O intermolecular distance which yields values of 1.74 \text{ A} for a bond order of two and 1.62 \text{ A} for a bond order of three. A value 1.74 \pm 0.05 \text{ A} was used.

The suggestion of Hewett et al.\(^7\) that the electronic structure of MoO should be closer to that of CrO than WO\(_3\) was followed in using the same treatment as for Mo\(_2^+\) where \( g = 3 \) was taken for the ground state and \( g < 5 \) for a low-excitation state in volume at 450 \text{ cm}^{-1}.

**References**

3. JANAF Thermochromical Tables, WO\(_3\) and WO\(_2\)(g), 9–30 (66).
Molybdenum Oxide (MoO₃)

CRYSTAL

Mₐ = 127.9388 Molybdenum Oxide (MoO₃)

Enthalpy of Formation

The adopted enthalpy of formation of MoO₃(cr) at 298.15 K is −140.5 ± 0.2 kcal mol⁻¹. This value is chosen so as to be in agreement with Brewer¹ who has performed a critical analysis of all data pertaining to the molybdenum-oxygen system. However, Brewer chose to adopt the value previously used by JANAF,¹⁴ a value which was derived as a weighted average of two calorimetric determinations and seven equilibrium studies, the latter results based on S²(298.15 K) = 11.95 kcal mol⁻¹. In revising the S²(298.15 K) value to 11.04 cal K⁻¹ mol⁻¹ in the tabulation, the enthalpy of formation should also be revised. With the exception of the data from Barbi² the following equilibrium studies suggest Δ_H^f(298.15 K) = −141.2 kcal mol⁻¹ in comparison with the calorimetric mean of Δ_H^f(298.15 K) = −140.8 kcal mol⁻¹ for MoO₃(cr). In addition, eight recent emf studies (published since the analysis by Brewer) also yield a value of Δ_H^f(298.15 K) = −141.2 kcal mol⁻¹. Although there is some overlap in the values for Δ_H^f derived from equilibrium and calorimetric studies, the equilibrium studies appear to be more negative by 0.4 kcal mol⁻¹. Brewer noted (in reference to Δ_H^f (298.15 K) = −140.5 kcal mol⁻¹) however, that a better overall fit of all Mo-O data would be obtained if the enthalpy of formation of MoO₃(cr) were made more negative by 0.5 kcal mol⁻¹ with a corresponding decrease of 0.5 kcal mol⁻¹ for MoO₃(g) and MoO₃(g) and 0.8 kcal mol⁻¹ for MoO₃(g). Such a change could be accommodated in the MoO₃ tables.

Ignition of the bomb from the calorimetric studies of Staskiewicz et al.³ indicated that oxidation was only about 70 percent complete. The authors also digested the products with NaOH to remove the trioxide. The residue was the dioxide, as indicated by both ignition and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah⁴ found 72–75 percent conversion to trioxide by weighing the total combustion products; no additional analysis was performed.

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
<th>Reaction</th>
<th>T(K)</th>
<th>Data Points</th>
<th>Δ_H^f(298.15 K), kcal mol⁻¹</th>
<th>Drift</th>
<th>Δ_H^f(298.15 K), kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staskiewicz et al.³</td>
<td>Calorimetric</td>
<td>A</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Mah⁴</td>
<td>Calorimetric</td>
<td>A</td>
<td>500</td>
<td>−37.52</td>
<td>−140.64 ± 0.13⁴</td>
<td>0</td>
<td>140.46 ± 0.13⁴</td>
</tr>
<tr>
<td>Rapp⁵</td>
<td>emf</td>
<td>B</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Barbi²</td>
<td>emf</td>
<td>C</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Greier and Chipman⁶</td>
<td>Equilibrium</td>
<td>D</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Gocken⁷</td>
<td>Equilibrium</td>
<td>E</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Collins⁸</td>
<td>Equilibrium</td>
<td>E</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
<tr>
<td>Torensod⁹</td>
<td>Equilibrium</td>
<td>E</td>
<td>500</td>
<td>−37.12</td>
<td>−140.86 ± 0.13⁴</td>
<td>0</td>
<td>140.26 ± 0.13⁴</td>
</tr>
</tbody>
</table>

**Auxiliary data for MoO₃(cr) are taken from corresponding measurements of the same authors. See also JANAF.¹³**

Reactions:

A. MoO₃(cr) + 1/2 O₂(g) = MoO₃(cr)

B. 2 Fe₂O₃(cr) + 3 MoO₃(cr) + 2 Fe(c) = 3 MoO₃(cr) + 2 Fe₂O₃(cr)

C. 2 NO(g) + MoO₃(cr) = MoO₃(cr) + 2 NO(g)

D. MoO₃(cr) + CO(g) = MoO₃(cr) + CO₂(g)

**Heat Capacity and Entropy**

King⁵ measured low temperature heat capacities from 53.3 to 296 K. King et al.¹⁰ measured the high temperature enthalpy changes from 399 to 1801 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they smooth at 298.15 K. Deviations of the enthalpy data from the adopted values are −1.3 to +0.7%, excluding the point at 1801 K. This point at the highest temperature deviates by +2.3%, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy S²(298.15 K) = 11.104 cal K⁻¹ mol⁻¹ is obtained from the low temperature heat capacity data, based on S²(1 K) = 0.36 cal K⁻¹ mol⁻¹. As discussed by Brewer, Ghose et al.¹² used neutron diffraction measurements to demonstrate the absence of a permanent magnetic moment. Thus no additional heat capacity or entropy contribution below 50 K due to a possible antiferromagnetic effect is necessary.

References


Continued on page 1598

---

Enthalphy Reference Temperature = Tₐ = 298.15 K

Enthalphy Reference Temperature = Tₐ = 298.15 K

Standard State Pressure = pₐ = 0.1 Ma

![Table](https://via.placeholder.com/150)

PREVIOUS: June 1967

CURRENT September 1978

---

Molybdenum Oxide (MoO₃)
Molybdenum Oxide (MoO₃)

IDEAL GAS

\[ M = 127.9388 \]

\[ \Delta H^\circ(0 \text{ K}) = 1157.294 \pm 20.9 \text{ kJ mol}^{-1} \]

\[ S^\ast(298.15 \text{ K}) = [276.990 \pm 8.4] \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H^\circ(298.15 \text{ K}) = -8.31 \pm 12.6 \text{ kJ mol}^{-1} \]

Vibrational Frequencies and Degeneracies

<table>
<thead>
<tr>
<th>( v ) (cm(^{-1}))</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>900 (1)</td>
<td>(3)</td>
</tr>
<tr>
<td>950 (1)</td>
<td></td>
</tr>
</tbody>
</table>

Electronic Levels and Quantum Weights

<table>
<thead>
<tr>
<th>( \epsilon ) (eV)</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(3)</td>
</tr>
<tr>
<td>13000</td>
<td>(6)</td>
</tr>
<tr>
<td>25000</td>
<td>(6)</td>
</tr>
</tbody>
</table>

Product of the Moments of Inertia: \( \mu d^2 = 5.663388 \times 10^{-12} \) g cm\(^2\)

Enthalpy of Formation

The adopted enthalpy of formation for MoO\(_3\)(g) at 298.15 K is \(-1.99 \pm 3\) kcal mol\(^{-1}\). This value was adopted by Brewer\(^1\) who has performed a critical analysis of all data pertaining to the molybdenum-oxygen system. Brewer\(^1\) adopted \( \Delta H^\circ(298.15 \text{ K}) \) R = 60700 ± 1500 K for the sublimation process MoO\(_2\)(cr) → MoO\(_3\)(g). The vapor pressures of MoO\(_3\) calculated from the tabulated slightly better than that obtained by Burns et al.\(^2\) and are 50% lower than those of Chizhikov et al.\(^3\). The adopted \( \Delta G^\circ(298.15 \text{ K}) \) values obtained from MoO\(_3\)(cr) and O\(_2\)(g) average 1 kcal mol\(^{-1}\) more negative than those determined by Franklin and Stickney.\(^1\) The only recent determination that deviates seriously is that of Belton and Wood\(^4\) who determined the volatility of molybdenum in steam-hydrogen mixtures at 1200 and 1500°C. The variation of their results with water partial pressure at 1383 to 1500°C indicate an incorrect correspondence to non-hydridic species which they attribute to MoO\(_4\) and MoO\(_3\). They assumed the ratio of MoO\(_3\) to MoO\(_2\) to be that observed by Burns et al.\(^2\) and obtained partial pressures of MoO\(_3\) about six times higher than calculated from the adopted values. Their values would require that \( \Delta H^\circ(298.15 \text{ K}) (\text{MoO}_3 + \text{O}_2(g)) \) be made more negative by 3200 K. If both \( \Delta H^\circ(298.15 \text{ K}) \) and \( \Delta G^\circ(298.15 \text{ K}) \) were shifted by their assigned uncertainties indicated, a change of 2000 K could be accommodated.

Burns et al.\(^2\) have investigated mass-spectrometrically the vapor in equilibrium with powdered MoO\(_3\)(cr) and also reported the partial pressures of MoO\(_3\)(g), MoO\(_2\)(g), and O\(_2\)(g) for MoO\(_3\)(cr). DeMaria et al.\(^5\) have measured the partial pressures of gaseous oxides MoO\(_3\), MoO\(_2\), and O\(_2\) in the Mo-O-AI system by mass spectrometry. Blackbum et al.\(^6\) and Plante\(^7\) have studied the vapor pressures above MoO\(_3\) (cr) by the Knudson effusion method. More recently there has been spectroscopic Kauernig cell studies of Chizhikov et al.\(^3\) of the vapor over MoO\(_4\)(cr) between 1500 and 1730 K and the Langmuir-type studies of Franklin and Stickney\(^1\) on the vapor resulting from oxides on a molybdenum surface.

Enthalpy Reference Temperature \( T_r = 298.15 \text{ K} \)

Standard State Pressure \( p^0 = 1 \text{ atm} \)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( C^* )</th>
<th>( S^* )</th>
<th>( H^\circ(T) )</th>
<th>( H^\circ(T_r) )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta G^\circ )</th>
<th>( \text{kg K}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>INFINITE</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Heat Capacity and Entropy

Hewett et al.\(^8\) have reviewed the spectroscopic studies on MoO\(_3\)(g). In addition they have studied spectroscopically MoO\(_3\) in neon and argon matrices at 4 K. The adopted bond distance and angle and two stretching frequencies are derived from this study. Brewer\(^1\) adopted the same values. The bending frequency (300 cm\(^{-1}\)) is estimated by comparison with other transition metal oxides.

Continued on page 1598
Molybdenum Oxide (MoO$_2$)

*CRYSTAL*

\[ M_r = 139.9384 \text{ Molybdenum Oxide (MoO}_2\text{)} \]

\[ \Delta H_f(0) = \text{Unknown} \]

\[ \Delta H_f(298.15 \text{ K}) = -708.41 \pm 3.3 \text{ kJ mol}^{-1} \]

\[ \Delta H_f = 0.0 \text{ kJ mol}^{-1} \]

**Enthalpy of Formation**

For this oxide, the atomic ratio of oxygen to molybdenum is 1.75 to 1 or 4/3. The formula MoO$_2$ is appropriate, and the tabulation is based on this ratio. The thermochemical values describing MoO$_2$ are approximately 1/4 those of MoO$_3$.

The high temperature enthalpy measurements of compositions between MoO$_2$ and MoO$_3$ gave widely divergent results, some of which are contradictory. The Mo-O phase diagram recommended by Brewer* Brewer* found that the phase diagram is not as simple as it seems to be, and that the more practical determination of \( \Delta H_f(298.15 \text{ K}) \) for MoO$_2$(cr) by fixing the thermodynamic properties of the peritectic equilibrium together with the thermodynamic data for the liquid. From the phase diagram, MoO$_2$ and MoO$_3$(cr) solids are in equilibrium with the peritectic liquid of 74.2 ± 0.1 atomic % oxygen at 1091 ± 7 K. For MoO$_3$(cr) = MoO$_2$(cr) + MoO$_3$(l), Brewer* obtained \( \Delta H_f = 0.863 \pm 0.03 \) at 1091 K. This yields, using auxiliary data, \( \Delta H_f = 1280 \pm 400 \text{ K} \) for the disproportionation of MoO$_3$ to crystalline MoO$_2$ and MoO$_3$ at 298.15 K. This heat of reaction yields \( \Delta H_f(298.15 \text{ K}) = -18520 \pm 200 \text{ K} \) from which we calculate \( \Delta H_f(298.15 \text{ K}) = -169.315 \pm 0.4 \text{ kcal mol}^{-1} \). We increase the uncertainty in \( \Delta H_f \) to ± 0.8 kcal mol$^{-1}$ which better represents the effect of errors in reducing a \( \Delta G^* \) value at 1091 K to a \( \Delta H_f \) value at 298.15 K.

**Heat Capacity and Entropy**

Bouquet et al.* used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for MoO$_3$(cr), MoO$_2$(cr), and MoO$_3$(cr). Brewer* compared their values of MoO$_3$(cr) and MoO$_3$(cr) mixtures with the same composition. For MoO$_3$(cr), the enthalpies were higher by 3% at 400 K, decreasing to 1.5% at 700 K. As these differences were within the scatter of the experimental measurements, Brewer* assumed \( \Delta C_P^* = 0 \) and \( \Delta S^* = 0 \) for the formation of MoO$_3$ from 3 MoO$_2$(cr) and MoO$_3$(cr). Bouquet et al.* also measured the high temperature enthalpy data of MoO$_3$ from 379 to 971 K. Their values agree with the adopted JANAF values for MoO$_3$ within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for MoO$_3$(cr), based on the assumptions for the higher temperatures as discussed in the preceding paragraph, may be less reliable at higher temperatures.

**Phase Data**

MoO$_3$(¢(p6m)) disproportionates to MoO$_3$ and liquid at 1091 ± 7 K, according to the phase diagram of Phillips and Chang. MoO$_3$(¢(p6m)) transforms on cooling below 875 ± 50 K to MoO$_2$(poly). Bouquet et al.* did not interpret their enthalpy data to include a transition at 875 K. However, a graphical examination of their data suggests two comments. First, the data point at 670 K may be a typographical error, perhaps 62.58 cal g$^{-1}$ should be 52.58 cal g$^{-1}$. Second, a transition at approximately 850 K with a corresponding heat of 0.7 kcal mol$^{-1}$ could be fairly consistent with Brewer*; we assume a transition at 875 ± 50 K with a corresponding zero heat of transition.

In addition to the discussion of the molybdenum oxides by Brewer,* Gmelin Handbuch der Anorganischen Chemie* has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases Ektrom and Tilley* have reviewed the work of Ekstrom as well as the earlier work of Kihlborg* on the phases in the Mo-O system.

**References**

5. JANAF Thermochemical Tables: MoO$_3$(cr) and MoO$_3$(l), 9-30-78.
Molybdenum Oxide (MoO$_2$) (cr)

\[ \Delta H^\circ(298.15 \text{ K}) = -727.13 \pm 2.5 \text{ kJ mol}^{-1} \]

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.875 or 23/8. The formula MoO$_2$ (upon which this tabulation is based) is more indicative of the oxygen content relative to Mo$_2$O$_5$ and MoO$_3$, as opposed to MoO$_2$. The thermochromic values describing MoO$_2$ are numerically 1/5 those of MoO$_3$.

The high temperature endm measurements$^{1,2,3}$ on compositions between MoO$_2$ and MoO$_3$ gave widely divergent results, some of which are contradicted by the Mo-O phase diagram recommended by Brewer$^4$. Brewer$^4$ found that it was more practical to determine a $\Delta H^\circ(298.15 \text{ K})$ value for MoO$_2$(cr) by fixing the thermodynamic properties from the peritectic equilibria together with the thermodynamic data for the liquid.

From the Mo-O phase diagram,$^1$ MoO$_2$(cr) and MoO$_3$(cr) solids are in equilibrium with the peritectic liquid of 74.40 ± 0.41 atomic % oxygen at 1058 ± 5 K. For the equilibrium MoO$_2$(cr) + 4 MoO$_2$(cr) + 2 MoO$_2$(cr), Brewer$^4$ calculated a $\Delta G^\circ(298.15 \text{ K})$ value of 105 K. This yielded, using auxiliary data,$^1$ a $\Delta H^\circ(298.15 \text{ K})$ value of 87454 ± 150 K from which we calculate $\Delta H^\circ(298.15 \text{ K}) = -173.788 ± 0.3 \text{ kJ mol}^{-1}$. This increase the uncertainty in $\Delta H^\circ(298.15 \text{ K})$, a value which better represents the effect of uncertainties in reducing a $\Delta G^\circ$ value at 1058 K to a $\Delta H^\circ$ value at 298.15 K.

Heat Capacity and Entropy

Bouquet et al.$^5$ used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for MoO$_2$(cr), MoO$_2$(cr), and MoO$_2$(cr) mixtures. For MoO$_2$(cr), the enthalpies were lower by 15% at 400 K, lower by 3% at 500 K, and higher at higher temperatures, becoming 6% high at 700 K. As these differences were within the scatter of the experimental measurements, Brewer$^4$ assumed $\Delta C_H^\circ = 0$ and $\Delta S^\circ = 0$ for the formation of MoO$_2$(cr) from 3MoO$_2$(cr) and MoO$_2$(cr).

Bouquet et al.$^5$ also measured high temperature enthalpy data of MoO$_2$ from 379 to 971 K. Their values agree with the adopted JANAFA values$^1$ for MoO$_2$(cr) within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for MoO$_2$(cr), based on the assumption $\Delta C_H^\circ = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data

The phase MoO$_2$(mp2) was found by Kihlborg$^6$ and Bouquet and Guillou$^7$ at temperatures up to 1058-1063 K. Bouquet and Guillou$^7$ observed MoO$_2$ disproportionated to MoO$_2$(cr) and MoO$_2$(cr) at 1053 K by differential thermal analysis. Brewer$^4$ adopted MoO$_2$ as a stable phase which disproportionates to MoO$_3$ and liquid at a temperature, $T_{99} = 1058 ± 5$ K, which is slightly above the disproportionation temperature of MoO$_3$.

In addition to the discussion of the molybdenum-oxide system by Brewer$^4$, Gmelin Handbook of Anorg anxious Chemie$^8$ has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley$^9$ have reviewed the work of Ekstrom as well as the earlier work of Kihlborg$^{10}$ in the phases on the Mo-O system.

References


$^5$JANAFA Thermochemical Tables: MoO$_2$(cr), MoO$_2$(cr), and MoO$_2$(s), 9-30-78.


Molybdenum Oxide (MoO$_2$)\textsubscript{cr}

**Crystalline**

$M_r = 142.1623$ Molybdenum Oxide (MoO$_2$)\textsubscript{cr}

<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature</th>
<th>$T_c$ (K)</th>
<th>$S$ (mol mol$^{-1}$)</th>
<th>$C_p$ (mol mol$^{-1}$ K$^{-1}$)</th>
<th>$H^*$ (mol mol$^{-1}$)</th>
<th>$G^*$ (mol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>298.15</td>
<td>72.772</td>
<td>74.281</td>
<td>0.0</td>
<td>-729.165</td>
</tr>
<tr>
<td>100</td>
<td>298.15</td>
<td>72.955</td>
<td>74.282</td>
<td>0.135</td>
<td>-729.153</td>
</tr>
<tr>
<td>200</td>
<td>298.15</td>
<td>80.923</td>
<td>74.282</td>
<td>8.855</td>
<td>-629.078</td>
</tr>
<tr>
<td>300</td>
<td>298.15</td>
<td>85.355</td>
<td>83.088</td>
<td>16.188</td>
<td>-604.456</td>
</tr>
<tr>
<td>400</td>
<td>298.15</td>
<td>89.487</td>
<td>89.543</td>
<td>24.940</td>
<td>-580.129</td>
</tr>
<tr>
<td>500</td>
<td>298.15</td>
<td>93.283</td>
<td>96.806</td>
<td>34.082</td>
<td>-556.082</td>
</tr>
<tr>
<td>600</td>
<td>298.15</td>
<td>97.415</td>
<td>103.700</td>
<td>43.621</td>
<td>-532.303</td>
</tr>
<tr>
<td>700</td>
<td>298.15</td>
<td>101.631</td>
<td>110.417</td>
<td>53.571</td>
<td>-508.790</td>
</tr>
<tr>
<td>800</td>
<td>298.15</td>
<td>105.973</td>
<td>116.922</td>
<td>63.649</td>
<td>-485.545</td>
</tr>
<tr>
<td>900</td>
<td>298.15</td>
<td>110.476</td>
<td>123.208</td>
<td>74.770</td>
<td>-462.273</td>
</tr>
<tr>
<td>1000</td>
<td>298.15</td>
<td>115.010</td>
<td>129.284</td>
<td>86.048</td>
<td>-439.879</td>
</tr>
<tr>
<td>1100</td>
<td>298.15</td>
<td>119.645</td>
<td>135.164</td>
<td>97.795</td>
<td>-417.470</td>
</tr>
<tr>
<td>1200</td>
<td>298.15</td>
<td>124.379</td>
<td>140.862</td>
<td>110.021</td>
<td>-395.331</td>
</tr>
<tr>
<td>1300</td>
<td>298.15</td>
<td>129.559</td>
<td>146.596</td>
<td>122.734</td>
<td>-373.528</td>
</tr>
</tbody>
</table>

**Heat Capacity and Entropy**

Bouquet et al. used differential enthalpy analysis to obtain enthalpies of 379 K for MoO$_2$(cr) and MoO$_2$(ct), and MoO$_2$(ct) and MoO$_2$(cr) of Brewer. Brewer compared their values with values of MoO$_2$(cr) and MoO$_2$(ct) mixtures with the same composition. For MoO$_2$(cr), the enthalpies were lower by 10% at 0 K than cross over between 500 and 600 K, and were 3% higher at 700 K. As these differences were within the scatter of the experimental measurements, Brewer assumed $\Delta C_p = 0$ and $\Delta S = 0$ for the formation of MoO$_2$(cr) from MoO$_2$(ct) and MoO$_2$.

Bouquet et al. also measured high temperature enthalpy of MoO$_2$ from 379 to 797 K. They also agreed with the adopted JANAF values for MoO$_2$(cr) within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 900 K. Thus, the adopted heat capacity values for MoO$_2$(cr), based on the assumption $\Delta C_p = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

**Phase Data**

MoO$_2$ (m⁷⁰) disproportionsates at 1053 ± 5 K to MoO$_2$ and liquid according to the phase diagram of Phillips and Chang. Brewer adopted a phase diagram which included MoO$_2$ which Phillips and Chang did not have. In addition to the discussion of the molybdenum-oxygen system by Brewer, Gmelin Handbuch der Anorganischen Chemie has recently presented a thorough survey of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley have reviewed the work of Ekstrom as well as the earlier work of Kilbarga on the phases in the Mo-O system.

**References**

5. JANAF Thermochemical Tables: MoO$_2$(cr), MoO$_2$(ct), and MoO$_2$(ct), 9–30–78.
Molybdenum Oxide (MoO₃)

\[ M = 143.9382 \]

CRYSTAL

**Enthalpy of Formation**

The adopted enthalpy of formation is \(-178.1 \text{ kcal mol}^{-1}\), the weighted average of two calorimetric determinations. The result of these and other calorimetric determinations, for all of the reaction \(\text{MoO}_3 + 3/2 \text{O}_2 \rightarrow \text{MoO}_3\), are given below. Staszkiewicz et al. found that oxidation was only about 80% complete and tentatively attributed this to formation of \(\text{MoO}_2\). Using their analytical results and their value of enthalpy of combustion for \(\text{MoO}_3\), we obtain \(\Delta H^{\circ}(\text{MoO}_3, \text{cr}) = 298.15 \text{ K}) = 177.98 \text{ kcal mol}^{-1}\). Subsequent discovery of oxides intermediate between \(\text{MoO}_3\) and \(\text{MoO}_2\) raises a possible uncertainty concerning the incompleteness of oxidation. Malz et al. reported that combustion of the \(\text{MoO}_3\) sample ranged from 84 to 93 percent complete, as determined only by weight gain of the total combustion products upon prolonged low temperature ignition. In contrast, the earlier workers reported almost complete combustion. Neumann et al. found 97% completion using a wet analysis involving aqua regia. Goose and Page found that in several combustions, they obtained over 99% completion, based on the weight of the oxide formed.

**Heat Capacity and Entropy**

Smith et al. measured low temperature heat capacities from 18.3 to 299.8 K. King et al. measured high temperature enthalpy data from 399.3 to 1063.9 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they join smoothly near 300 K. Deviations of the enthalpy data from the adopted values are \(-6.5\%\) to \(+12\%\). Selz et al. have also measured low temperature heat capacities from 70 to 298.7 K which are in agreement with the values adopted. The discrepancy has been discussed by Smith, Cosgrove and Snyder measured high temperature enthalpy data from 273 to 1068 K by drop calorimetry. Their smooth values are about 2\% higher than the values adopted in the tabulation. Bouquet et al. also measured high temperature enthalpy data from 379 to 971 K. Their values agree with the adopted values within \(2\%\) below 300 K, but the deviations increase rapidly at higher temperature becoming \(+10\%\) at 950 K.

The entropy, \(S^{\circ}(298.15 \text{ K}) = 18.585 \text{ cal K}^{-1} \text{ mol}^{-1}\), is obtained from the low temperature heat capacity data of Smith et al., based on \(S^{\circ}(298.15 \text{ K}) = 18.585 \text{ cal K}^{-1} \text{ mol}^{-1}\). This starting entropy was obtained by the authors from a 7º extrapolation of the data. Recently, McBride and Westrum have shown that the 7º extrapolation is inappropriate for \(\text{MoO}_2\) and a 7º law is suggested for this and other compounds with lamellar lattices. They have also shown that the enthalpy data of Smith et al. for \(\text{MoO}_2\) was positively biased by \(-0.03 \text{ cal K}^{-1} \text{ mol}^{-1}\) below 100 K. If the same bias is present in the \(C_p\) data of Smith et al., for \(\text{MoO}_3\), and a 7º extrapolation is used, our analysis suggests a reduction of \(-0.03 \text{ cal K}^{-1} \text{ mol}^{-1}\) in \(S^{\circ}(298.15 \text{ K})\). Other treatments result in estimated decreases in \(S^{\circ}(298.15 \text{ K})\) ranging from 0.08 to 0.17 cal K\(^{-1}\) mol\(^{-1}\). The increasing scatter in the \(C_p\) data below 40 K (indicative of a loss of calorimeter sensitivity) coupled with uncertainty due to bias suggests an uncertainty of \(\pm 0.3 \text{ cal K}^{-1} \text{ mol}^{-1}\) for \(S^{\circ}(298.15 \text{ K})\). Therefore, we adopt the authors' original interpretation recognizing the need for new low temperature \(C_p\) measurements. It is surprising that the entropy of \(\text{MoO}_3\) is lower than that of \(\text{WO}_3\) by about 0.4 cal K\(^{-1}\) mol\(^{-1}\). This may be due to the difference in the crystal structures, \(\text{MoO}_3\) being orthorhombic (a\(^{16}\)) and \(\text{WO}_3\) monoclinic, and also to uncertainty in the entropy extrapolation below 50 K for \(\text{WO}_3\).

**Fusion Data**

The adopted melting point, 1074 ± 5 K, is obtained from King et al. The enthalpy of fusion is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King. Cosgrove and Snyder found the melting point 1068 K by the cooling curve method and derived \(\Delta H^{\circ}(\text{fus}) = 125.4 \text{ kcal mol}^{-1}\) from their smooth enthalpy values at the melting point.

**References**

Molybdenum Oxide (MoO₃)

LIQUID

\[ M_r = 143.9382 \]  

\[ \Delta H^r(298.15 \text{ K}) = \{-703.727\} \text{ kJ-mol}^{-1} \]

\[ \Delta S^r(298.15 \text{ K}) = 45.534 \pm 2.4 \text{ kJ-K}^{-1} \text{-mol}^{-1} \]

\[ T_m = 1074 \pm 5 \text{ K} \]

Enthalpy of Formation

\( \Delta H_r^f(\text{MoO}_3, l, 298.15 \text{ K}) \) is calculated from that of the crystal by adding the enthalpy of fusion, \( \Delta_mH^f \), and the difference in enthalpy, \( H^r(1074 \text{ K}) - H^r(298.15 \text{ K}) \), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the enthalpy data (1074-1392 K) measured by King et al. The heat capacity is assumed constant above and below the measured range. At 750 K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. \( S^* \text{(MoO}_3, l, 298.15 \text{ K}) \) is calculated in a manner analogous to that used for the enthalpy of formation.

Coxgrove and Snyder also measured enthalpy data for MoO₃(l) in the temperature range from 1068 to 1300 K. Their smooth values are 2.5 to 4.0 percent higher than our tabulated values.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Effusion and transpiration measurements indicate that MoO₃(g) is not the major species found in the vapor above MoO₃ condensed phases. Both sets of measurements indicate the presence of polymeric species (MoO₃), where the predominant species near the normal boiling point are those for \( x = 3 \) and 4. At higher temperatures the equilibrium shifts toward lower \( x \) but MoO₃(l) will reach 1 atm at 1380 ± 30 K based primarily on the vapor pressures of Ackermann et al. using indirect methods, reported a normal boiling point of 1438 K. We adopt Brewer's estimate and emphasize that this represents vaporization to a mixture of gases, (MoO₃).

References


<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature = ( T_r = 298.15 \text{ K} )</th>
<th>Standard State Pressure = ( p^* = 0.1 \text{ MPa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T/K )</td>
<td>( C_r^* )</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>298.15</td>
</tr>
<tr>
<td>300</td>
<td>75.107</td>
</tr>
<tr>
<td>325</td>
<td>83.054</td>
</tr>
<tr>
<td>500</td>
<td>87.751</td>
</tr>
<tr>
<td>600</td>
<td>91.776</td>
</tr>
<tr>
<td>700</td>
<td>93.814</td>
</tr>
<tr>
<td>750.000</td>
<td>96.896</td>
</tr>
<tr>
<td>750.000</td>
<td>126.951</td>
</tr>
<tr>
<td>1000</td>
<td>126.951</td>
</tr>
<tr>
<td>1200</td>
<td>126.951</td>
</tr>
<tr>
<td>1500</td>
<td>126.951</td>
</tr>
<tr>
<td>1074</td>
<td>126.951</td>
</tr>
<tr>
<td>1100</td>
<td>126.951</td>
</tr>
<tr>
<td>1400</td>
<td>126.951</td>
</tr>
<tr>
<td>1500</td>
<td>126.951</td>
</tr>
<tr>
<td>1600</td>
<td>126.951</td>
</tr>
<tr>
<td>1700</td>
<td>126.951</td>
</tr>
<tr>
<td>1800</td>
<td>126.951</td>
</tr>
<tr>
<td>1900</td>
<td>126.951</td>
</tr>
</tbody>
</table>

PREVIOUS: June 1967  CURRENT: September 1978
Molybdenum Oxide (MoO₃)  

<table>
<thead>
<tr>
<th>T/K</th>
<th>C°</th>
<th>S°</th>
<th>ΔH°</th>
<th>ΔG°</th>
<th>log Kᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>INFINITE</td>
<td>-12.590</td>
<td>-740.150</td>
<td>INFINITE</td>
</tr>
<tr>
<td>200</td>
<td>59.279</td>
<td>50.977</td>
<td>84.136</td>
<td>-6.623</td>
<td>-745.249</td>
</tr>
<tr>
<td>298.15</td>
<td>74.881</td>
<td>77.760</td>
<td>77.760</td>
<td>0.0</td>
<td>-745.170</td>
</tr>
<tr>
<td>300</td>
<td>75.107</td>
<td>78.224</td>
<td>77.761</td>
<td>0.139</td>
<td>-745.138</td>
</tr>
<tr>
<td>400</td>
<td>83.094</td>
<td>101.565</td>
<td>80.821</td>
<td>8.098</td>
<td>-744.111</td>
</tr>
<tr>
<td>500</td>
<td>87.751</td>
<td>120.130</td>
<td>86.820</td>
<td>16.630</td>
<td>-742.696</td>
</tr>
<tr>
<td>600</td>
<td>91.776</td>
<td>136.467</td>
<td>93.775</td>
<td>25.627</td>
<td>-741.074</td>
</tr>
<tr>
<td>700</td>
<td>95.814</td>
<td>150.936</td>
<td>100.927</td>
<td>33.066</td>
<td>-739.250</td>
</tr>
<tr>
<td>800</td>
<td>85.031</td>
<td>164.033</td>
<td>108.087</td>
<td>44.796</td>
<td>-737.186</td>
</tr>
<tr>
<td>900</td>
<td>104.441</td>
<td>176.037</td>
<td>114.905</td>
<td>55.018</td>
<td>-734.839</td>
</tr>
<tr>
<td>1000</td>
<td>109.039</td>
<td>187.278</td>
<td>121.387</td>
<td>65.651</td>
<td>-732.172</td>
</tr>
<tr>
<td>1074.000</td>
<td>112.562</td>
<td>195.186</td>
<td>126.387</td>
<td>73.889</td>
<td>--</td>
</tr>
<tr>
<td>1074.000</td>
<td>126.951</td>
<td>240.376</td>
<td>126.387</td>
<td>122.424</td>
<td>--</td>
</tr>
</tbody>
</table>

**Enthalpy Reference Temperature = T₀ = 298.15 K**

**Standard State Pressure = p* = 0.1 MPa**

**M = 143.9382**  

---

**PREVIOUS.**  

**CURRENT: September 1978**

---

MALCOLM W. CHASE
### Molybdenum Oxide (MoO₃)

**IDEAL GAS**

\[
\Delta H^{\text{p}}(T) = 140.125 \pm 21.3 \text{ kJ mol}^{-1}
\]

\[
S^{\text{f}}(298.15 \text{ K}) = (283.8) \pm (12.6) \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
\Delta H^{\text{p}}(298.15 \text{ K}) = -346.44 \pm 20.9 \text{ kJ mol}^{-1}
\]

#### Vibrational Frequencies and Degeneracies

<table>
<thead>
<tr>
<th>ν, cm⁻¹</th>
<th>ν₀, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>978 (1)</td>
<td>974 (2)</td>
</tr>
<tr>
<td>(2940)</td>
<td>(3010)</td>
</tr>
</tbody>
</table>

**Ground State Quantum Weight:** 1

**Point Group:** C₃v

**Bond Distance:** Mo-O = 1.73 Å

**Bond Angle:** Mo-O-Mo = 90°

**Product of the Moments of Inertia:** \( I_{\text{G}} = 3(0.07222 \times 10^{-44}) \) g cm²

### Enthalpy of Formation

Burns et al. determined the partial pressures of gaseous oxides MoO₃, MoO₂, Mo₂O₃, and Mo₃O₄ in equilibrium with powdered MoO₃ by spectrometric measurements. Blackburn et al. and Chikizhikov et al. also investigated the vapor pressures above molybdenum dioxide by the Knudsen effusion method. These studies involve the disproportionation of Mo(0) to Mo(0) and Mo(0)₃. DeMaris et al. reported the partial pressures of MoO(0), MoO₂(0), MoO₃(0), and Mo₃O₄(0) in the Mo₃O₄-Al₂O₃ system from mass spectrometry.

### Source, Reaction, Data Points, Drift (cal·K⁻¹·mol⁻¹), ΔHₚ(298.15 K), kcal·mol⁻¹

<table>
<thead>
<tr>
<th>Source</th>
<th>Reaction</th>
<th>T/K</th>
<th>Data Points</th>
<th>ΔHₚ(298.15 K), kcal·mol⁻¹</th>
<th>Drift (cal·K⁻¹·mol⁻¹)</th>
<th>ΔHₚ(298.15 K) kcal·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 MoO(cr) → MoO(g) + 0.5 Mo(cr)</td>
<td>1481-1777</td>
<td>34</td>
<td>151.7 ± 1.5</td>
<td>128.0 ± 0.8</td>
<td>2.2 ± 0.9</td>
<td>-82.8</td>
</tr>
<tr>
<td>1.5 MoO(cr) + 0.5 MoO(cr) → MoO₂(cr)</td>
<td>1592-1918</td>
<td>119</td>
<td>133.5 ± 1.4</td>
<td>124.0 ± 1.3</td>
<td>6.3 ± 0.8</td>
<td>-88.6</td>
</tr>
<tr>
<td>1.5 MoO(cr) + 0.5 MoO(cr) + 0.5 Mo(cr)</td>
<td>1818-2028</td>
<td>7</td>
<td>108.8 ± 6.4</td>
<td>121.2 ± 1.6</td>
<td>6.3 ± 3.4</td>
<td>-89.5</td>
</tr>
<tr>
<td>1.5 MoO(cr) + 0.5 MoO(cr) → MoO₂(cr)</td>
<td>1500-1700</td>
<td>139</td>
<td>133.1 ± 0.5</td>
<td>0.0</td>
<td>3.0</td>
<td>-77.6</td>
</tr>
<tr>
<td>Mo(cr) + 3 O(cr)</td>
<td>228-2416</td>
<td>6</td>
<td>-210.5 ± 28.3</td>
<td>-253.7 ± 4.0</td>
<td>-18.6 ± 11.8</td>
<td>-75.0</td>
</tr>
</tbody>
</table>

The selected enthalpy of formation is -82.8 kcal·mol⁻¹, based on the 3rd law value of ΔHₚ(298.15 K) of Burns et al. The choice is made because there is serious doubt about the data of Blackburn et al. as discussed by Burns et al. In addition, the assumptions made by Plante are not very reliable since they only apply to species of any importance in MoO₃, which are not real. The mechanical work of Burns et al. is thus preferred. The heat of formation calculated from the JANAF tables is ΔHₚ(T) = 415.9 ± 5.1 kcal·mol⁻¹.

### Heat Capacity and Entropy

In a recent IR matrix isolation study, Hewat et al. observed peaks at 972 and 992 cm⁻¹ assigned to MoO₂(0) and MoO₃(0), which are shifted towards stretching modes of MoO₃(g). We add 2 cm⁻¹ to these frequencies to correct for the matrix effect. The observation of two stretching modes in the infrared spectrum suggests a pyramidal C₃v structure for MoO₃. Hewat et al. performed a normal coordinate analysis using a bond distance of 1.8 Å and an estimated bending force constant \( k = 0.296 \text{ mdyn\AA} \). Variations of 20% in \( k \) changed the calculated stretching frequencies by only a few cm⁻¹. The calculated stretching frequencies were more sensitive to the estimated pyramidal angle \( \theta \) which was adjusted to obtain the best fit to the observed stretching frequencies of oxide molecules containing \( \text{O}_2 \text{O} \); O, and mixed \( \text{O}_2 \text{O} \). The final results yielded \( \theta = 65.1 ± 2 \text{°} \) and values of 261, 275, and 375 Å for the bending frequencies of MoO₃. Due to the insensitivity of the normal coordinate analysis to \( \theta \), these bending frequencies are useful only for comparing changes due to isotopic substitution. In contrast, we adopt bending frequencies of 310, 310 and 340 cm⁻¹ and a bond distance of 1.73 Å as selected by Brewer for consistency with other metal oxides.

The pyramidal angle of 65.1° is adopted, the possible effect of using a shorter bond distance during the normal coordinate analysis is unknown. The pyramidal angle of 65.1° corresponds to an O-Mo-O bond angle of 90°. Based on the adopted structure, the principal moments of inertia are \( I_{xx} = (12.3872 \times 10^{-45}) \) g cm² and \( I_{yy} = (18.3909 \times 10^{-45}) \) g cm². The thermodynamic functions are consistent with those of Brewer.

### References


**PREVIOUS:** September 1978 (1st ed)

**CURRENT:** September 1978 (1st ed)
<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature</th>
<th>$T_r = 298.15$ K</th>
<th>Standard State Pressure</th>
<th>$p_s = 0.1$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta f^\text{r} H_m R$</td>
<td>$\Delta f^\text{f} H_m R$</td>
<td>$\Delta f^\text{r} H_m$</td>
<td>$\Delta f^\text{f} H_m$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>$-10.579$</td>
<td>$-273.314$</td>
</tr>
<tr>
<td>100</td>
<td>24.050</td>
<td>12.991</td>
<td>110.098</td>
</tr>
<tr>
<td>200</td>
<td>51.840</td>
<td>39.359</td>
<td>268.090</td>
</tr>
<tr>
<td>298.15</td>
<td>63.555</td>
<td>62.572</td>
<td>62.572</td>
</tr>
<tr>
<td>300</td>
<td>63.680</td>
<td>62.965</td>
<td>62.573</td>
</tr>
<tr>
<td>400</td>
<td>68.910</td>
<td>82.099</td>
<td>65.146</td>
</tr>
<tr>
<td>500</td>
<td>71.756</td>
<td>97.805</td>
<td>70.155</td>
</tr>
<tr>
<td>600</td>
<td>73.597</td>
<td>111.057</td>
<td>75.897</td>
</tr>
<tr>
<td>700</td>
<td>75.019</td>
<td>122.511</td>
<td>81.756</td>
</tr>
<tr>
<td>800</td>
<td>76.233</td>
<td>132.610</td>
<td>87.494</td>
</tr>
<tr>
<td>900</td>
<td>77.278</td>
<td>141.650</td>
<td>93.018</td>
</tr>
<tr>
<td>1000</td>
<td>78.241</td>
<td>149.842</td>
<td>98.297</td>
</tr>
<tr>
<td>1300</td>
<td>80.833</td>
<td>170.699</td>
<td>112.691</td>
</tr>
<tr>
<td>1400</td>
<td>81.672</td>
<td>176.721</td>
<td>117.053</td>
</tr>
<tr>
<td>1500</td>
<td>82.467</td>
<td>182.383</td>
<td>121.220</td>
</tr>
<tr>
<td>1600</td>
<td>83.262</td>
<td>187.730</td>
<td>125.211</td>
</tr>
<tr>
<td>1700</td>
<td>84.057</td>
<td>192.802</td>
<td>129.039</td>
</tr>
<tr>
<td>1800</td>
<td>84.810</td>
<td>197.628</td>
<td>132.717</td>
</tr>
<tr>
<td>1900</td>
<td>85.555</td>
<td>203.235</td>
<td>136.255</td>
</tr>
<tr>
<td>2100</td>
<td>87.111</td>
<td>216.076</td>
<td>142.956</td>
</tr>
<tr>
<td>2200</td>
<td>87.906</td>
<td>214.947</td>
<td>146.137</td>
</tr>
<tr>
<td>2300</td>
<td>88.659</td>
<td>218.871</td>
<td>149.214</td>
</tr>
<tr>
<td>2400</td>
<td>89.412</td>
<td>222.060</td>
<td>152.196</td>
</tr>
</tbody>
</table>

References
4. JANAF Thermochimical Tables: O(g), 3–317; SO(g), 6–30–61.
Molybdenum Sulfide (MoS₂)

\[ \Delta H^\circ(0 \text{ K}) = 407.103 \pm 8.4 \text{ kJ mol}^{-1} \]
\[ \Delta H^\circ(298.15 \text{ K}) = -129.704 \pm 41.8 \text{ kJ mol}^{-1} \]

**Enthalpy of Formation**

The adopted enthalpy of formation is taken from the critical review by Brewer.\(^1\) His linear regression analysis of equilibrium data, which is based on Cubicotti's sigma-plot method,\(^2\) yields both \(\Delta H^\circ(298.15 \text{ K})\) and \(\Delta S^\circ(298.15 \text{ K})\). The data used in Brewer's analysis are outlined below. Auxiliary data are taken from the JANAF tables.\(^3\)

<table>
<thead>
<tr>
<th>Source</th>
<th>Reaction</th>
<th>T/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>McCabe(^4)</td>
<td>A</td>
<td>1303 – 1425</td>
</tr>
<tr>
<td>Isaković(^5)</td>
<td>B</td>
<td>1523 – 1738</td>
</tr>
<tr>
<td>Hager and Elliott(^6)</td>
<td>C</td>
<td>1366 – 1612</td>
</tr>
<tr>
<td>Stubbles and Richardson(^7)</td>
<td>C</td>
<td>1119 – 1467</td>
</tr>
<tr>
<td>Pouillard and Perrot(^8)</td>
<td>C</td>
<td>1030 – 1280</td>
</tr>
</tbody>
</table>

**Heat Capacity and Entropy**

There are no experimental high temperature heat capacity or enthalpy studies. The adopted heat capacity, which is assumed to represent the high temperature crystal form, is based on the estimate of Gruenvold and Westrum,\(^9\) \(C_P^\circ = 26.3 + 7.88 \times 10^{-7} \text{T} - 2.30 \times 10^{-7} \text{T}^2\). The value of \(\Delta S^\circ(298.15 \text{ K})\) is taken from Brewer,\(^1\) refer above.

Rastogi and Ray\(^10\) measured the low temperature \(C_P^\circ(350 \text{ K})\) but report only \(C_P^\circ(298.15 \text{ K}) = 33.2 \text{ cal K}^{-1} \text{ mol}^{-1}\). This value apparently refers to the low temperature superstructure crystal form but is not expected to differ significantly from the high temperature form. The reason for the \(7 \text{ cal K}^{-1} \text{ mol}^{-1}\) discrepancy between the Rastogi–Ray value of \(C_P^\circ(298.15 \text{ K})\) and that adopted here is not known but it should be mentioned that the Rastogi–Ray value is well above the classical limit of 15 R. Insufficient information on sample preparation and calorimetric technique is available to assess the validity of the Rastogi–Ray data.

**Phase Data**

The crystal structure of MoS₂ is monoclinic and belongs to space group P2₁/m above 310 K.\(^11\) Below 310 K all axes are doubled and a superstructure is formed. The heat of transition is reported to be 5 cal K⁻¹ mol⁻¹.

The stability region for MoS₂ is from 900 ± 40 K to the melting point. Below 900 K the material is metastable with respect to disproportionation to Mo and (Mo₃S₄). However equilibrium is established very slowly below 1100 K,\(^12\) and, once prepared, MoS₂ may be quenched and stored indefinitely at room temperature. The enthalpy of decomposition at 900 K (\(\Delta H^\circ(900 \text{ K})\)) for the reaction MoS₂(cr) → 1/2 Mo(s) + 3/2 S₂(g) is calculated from the JANAF tables.\(^3\)

**Fusion Data**

We adopt the congruent melting point of Brewer.\(^1\) The enthalpy of fusion is estimated assuming an entropy of fusion of ~3 cal K⁻¹ mol⁻¹ as suggested by Kubaschewski et al.\(^13\) This gives a enthalpy of fusion of 31 kcal mol⁻¹ and the uncertainty is estimated to be 10 kcal mol⁻¹.

**References**

3. JANAF Thermochemical Tables: Mo(cr) 3–31–78; MoS₂(cr) 6–30–78; S₂(g) 9–30–77; H₂S(g) 6–30–77.
Molybdenum Sulfide (MoS₂)  LIQUID  \( M_f = 288.06 \)  Molybdenum Sulfide (MoS₂)  MoS₂(l)

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( C_f^2 )</th>
<th>( S^e/(\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) )</th>
<th>( H_f'/(\text{cal} \cdot \text{mol}^{-1}) )</th>
<th>( G_f'/(\text{cal} \cdot \text{mol}^{-1}) )</th>
<th>( \log K_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>200</td>
<td>298.15</td>
<td>109.924</td>
<td>181.170</td>
</tr>
<tr>
<td>300</td>
<td>109.489</td>
<td>181.847</td>
<td>181.172</td>
<td>0.220</td>
<td>-270.316</td>
</tr>
<tr>
<td>400</td>
<td>117.464</td>
<td>214.533</td>
<td>181.375</td>
<td>11.583</td>
<td>-277.627</td>
</tr>
<tr>
<td>600</td>
<td>127.399</td>
<td>264.175</td>
<td>203.948</td>
<td>36.136</td>
<td>-283.953</td>
</tr>
<tr>
<td>700</td>
<td>131.405</td>
<td>284.139</td>
<td>214.006</td>
<td>49.079</td>
<td>-283.396</td>
</tr>
<tr>
<td>800</td>
<td>135.162</td>
<td>301.913</td>
<td>223.901</td>
<td>62.409</td>
<td>-290.142</td>
</tr>
<tr>
<td>900</td>
<td>138.775</td>
<td>318.042</td>
<td>233.479</td>
<td>76.107</td>
<td>-290.748</td>
</tr>
<tr>
<td>1000</td>
<td>142.297</td>
<td>332.846</td>
<td>242.685</td>
<td>90.181</td>
<td>-297.887</td>
</tr>
<tr>
<td>1100</td>
<td>145.762</td>
<td>346.572</td>
<td>251.513</td>
<td>105.364</td>
<td>-304.824</td>
</tr>
<tr>
<td>1200</td>
<td>149.186</td>
<td>359.402</td>
<td>259.973</td>
<td>119.312</td>
<td>-311.574</td>
</tr>
<tr>
<td>1300</td>
<td>152.582</td>
<td>371.477</td>
<td>268.092</td>
<td>134.401</td>
<td>-318.155</td>
</tr>
<tr>
<td>1400</td>
<td>155.937</td>
<td>382.906</td>
<td>273.899</td>
<td>149.288</td>
<td>-334.582</td>
</tr>
<tr>
<td>1500</td>
<td>159.269</td>
<td>394.401</td>
<td>279.674</td>
<td>164.668</td>
<td>-416.612</td>
</tr>
<tr>
<td>1600</td>
<td>162.570</td>
<td>405.002</td>
<td>284.338</td>
<td>175.513</td>
<td>-430.947</td>
</tr>
<tr>
<td>1700</td>
<td>165.838</td>
<td>415.356</td>
<td>290.034</td>
<td>181.203</td>
<td>-427.516</td>
</tr>
<tr>
<td>1800</td>
<td>169.062</td>
<td>422.236</td>
<td>297.048</td>
<td>196.893</td>
<td>-424.305</td>
</tr>
<tr>
<td>1900</td>
<td>172.249</td>
<td>428.159</td>
<td>304.234</td>
<td>212.583</td>
<td>-421.327</td>
</tr>
<tr>
<td>2000</td>
<td>175.396</td>
<td>433.819</td>
<td>310.676</td>
<td>228.273</td>
<td>-418.594</td>
</tr>
<tr>
<td>2100</td>
<td>178.504</td>
<td>439.367</td>
<td>316.836</td>
<td>243.963</td>
<td>-416.121</td>
</tr>
</tbody>
</table>

References
1JANAF Thermochanical Tables: MoS₂(s) 6–30–78.
### Molybdenum Sulfide (MoS₂)

**CRYSTAL-LIQUID**

M₀ = 288.06  Molybdenum Sulfide (MoS₂)  MoS₂(cr,J)

<table>
<thead>
<tr>
<th>Enthalpy Reference Temperature T₀ = 298.15 K</th>
<th>Standard State Pressure p° = 0.1 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>C₀</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

*This material is reported to be metastable with respect to disproportionation to Mo(cr) and MoS₂(cr) below 900 K. However, disproportionation is very slow and the material may be quenched and stored at room temperature indefinitely.*

### NIST-JANAF Thermochemical Tables

**J. Phys. Chem. Ref. Data, Monograph 9**

PREVIOUS.  CURRENT: June 1978

Molybdenum Sulfide (MoS₂)  MoS₂(cr,J)
Continued from Page 1585

8. JANAF Thermochemical Tables, MoO$_4$(cr), 9-30-78.

Continued from Page 1586

The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod on WO$_3$.

The ground state is assumed to be $^1A_1$, and the first excited level is assumed to lie close to the observed transitions at 7890 Å and 7806 Å in WO$_3$. Since both these states are presumed to be triplet, we have assigned a total degeneracy of 6. In addition, we expect from the electronic levels of Mo$^{4+}$(g) that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm$^{-1}$. The principal moments of inertia are: $I_a = 3.3489 \times 10^{-39}$, $I_b = 11.4373 \times 10^{-39}$, and $I_c = 14.7862 \times 10^{-39}$ g cm$^2$.

References