CURRENT

PREVIOUS: December 1961 (1 atm

Potassium (K)

DEAL GAS

A_r = 39.0983 Potassium (K)

K₁(ref)

REFERENCE STATE

336.35 K crystal 1039.540 K liquid 1039.540 K ideal monatomic gas

5 5

Refer to the individual tables for details.

Potassium (K)

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

K₁(cr)

Potassium (K)

1466	5					MALCO	DLM W. CHASE	
K ₁ (cr)	- 0.1 MPa log Kr	ರಂಧ					, , , , , , , , , , , , , , , , , , ,	ember 1961
	Standard State Pressure = p° = 0.1 MPa $_{\rm A}$ $_{\rm A}$ $_{\rm C}$ $_{\rm A}$ $_{\rm C}$ $_{\rm C}$ $_{\rm C}$ $_{\rm C}$ $_{\rm C}$ $_{\rm C}$	ರಿರರ	0. 0. 0. L<> LIQUID 0.094 -					CURRENT December 1961
		ರರರ	0. 0. 0. CRYSTAL -2.275 -1.593					
	K H*-H*(T,)	-7.082 -5.350 -2.755	-1.381 0. 0.055 1.174 1.671 3.940					
	Enthalpy Reference Temperature - T. = 298.15 K T. C. S - [G - H'(T)] T T. C. S - [G - H'(T)] T	INFINITE 89 101 67.270	65 146 64.670 64.671 65.044 66.008					
	J.K ⁻¹ mol ⁻¹ S* -[G*	35 603 53.493						
т (Я)	Reference To	0. 24.631 27.004						
Potassium (K)	Enthalpy T/K	°888	250 298.15 300 336.350 350 400					PREVIOUS
A, = 39.0983	$\Delta_t H^o(0 \text{K}) = 0 \text{KJ} \cdot \text{mol}^{-1}$ $\Delta_t H^o(228 \text{IS} \text{K}) = 0 \text{kJ} \cdot \text{mol}^{-1}$ $\Delta_{tas} H^o = 2.334 \text{kJ} \cdot \text{mol}^{-1}$		JK),¹ Krier, Craig, and Wallace (12-320 K),² Eastman and Rodebush, (70-290 K)³ A smooth bree references. Above 300 K, the heat capacity			214 (1955). (1952).		
CRYSTAL			Heat Capacity and Entropty Low temperature heat capacity measurements have been reported by Roberts (1.5 20 K), ¹ Krier, Craig, and Wallace (12–320 K), ² Dauphinee, Martin, and Preston Thomas (20–330 K), ¹ Simon and Zeidler (15–300 K), ⁴ and Eastman and Rodebush, (70–290 K) A smooth curve was drawn through a large scale plot of the data, giving the most weight to the first three references. Above 300 K, the heat capacity data were adjusted to join smoothly with the enthalpy measurements of Douglas et al. ⁶	alpy measurements of Douglas et al.6	letails.	References ¹ L. M. Roberts, Proc. Phys. Soc. (London) 70B, 744 (1957). ² C. A. Krier, R. S. Craig, and W. E. Wallace, J. Phys. Chem. 61, 522 (1957). ³ T. M. Dauphinee, D. L. Martin, and H. Preston Thomas, Proc. Roy. Soc. (London) A233, 214 (1955). ⁴ F. Simon and W. Zeidler, Z. Physik. Chem. 123, 383 (1926). ⁵ E. D. Eastman and W. H. Rodebush, J. Am. Chem. Soc. 40, 489 (1918). ⁶ T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952).		
Potassium (K)	$S^{\circ}(298.15 \text{ K}) = 64.67 \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ $T_{\text{tot}} = 336.35 \text{ K}$	Enthalpy of Formation Zero by definition.	Heat Capacity and Entropty Low temperature heat capacity measun Dauphinee, Martin, and Preston Thomas (2 curve was drawn through a large scale plot data were adjusted to join smoothly with th	Fusion Data The enthalpy of fusion is from the enthalpy measurements of Douglas et al. 6	Sublimation Data R ₂ (g) tables for details.	References 1. M. Roberts, Proc. Phys. Soc. (London) 2. A. Krier, R. S. Craig, and W. E. Walla 2. M. Dauphinee, D. L. Martin, and H. Pr 4. Simon and W. Zeidler, Z. Physik. Cher 5. D. Eastman and W. H. Rodebush, J. Au 7. B. Douglas, A. F. Ball, D. C. Ginnings		

Vaporization Data

Potassium (K)

Potassium (K)

Refer to the individual tables for details.

0 to 336.35 K crystal above 336.35 K liquid

		1-1-m-1-17.1			1		•
τÆ	ប	S -[G	-[G*-H*(T,)]/T	H*-H*(T,)	A.II.	Φ'Q.	log Kr
۰8	0. 24.631	0. 35.603	INFINITE 89.101	-7.082 -5.350	o' o'	00	ರ ರ
88 88 88	28.008	53.493 59.623	67.270 65.146	-2.755 -1.381	o o	o o	ರ ರ
298.15	29.497	64.670	64.670	0.	o o	0 0	o o
336.3150	34.567	68.370	64.880	1.174	YST	> ,	- 1
85.0	31.993	76.586	65.312	3946	o'c	0.0	o o
8	31.067	84510	68.739	7.097	်ဝံ	်ဝံ	jo
88	30.695	87.763 93.306	73.482	8.54 14.08	0 0	o' c	0 0
88	29.824	27.92	76.960	14.676	Ö	ó	ဗ်
38	29 936	105.413	82.485	20.636	o' c	o' c	o' c
0001	30,361	108.587	84 939	23.648	o	; o	်ဝံ
1039.540	30.604	109.769	85.861	24.854 -	FUG	FUGACITY - 1 bar	- 1
98	31.031	1115111	87.223	26.716	-78.951	4.610	-0.219
38	32.803	116.835	91.377	29.862 33.096	-77.884	12.160	-0.529
6 6 8 8	33.723 34.644	119.300	93.284	36.422	-75.482	26 982	-1.007
9							

ප්ප්රේජ ප්ප්ර්ප්ජ ජප්ප්රේජ ප්ප්රේජ ප්ප්රේජ ප්ප්රේජ ප්ර්රේජ ප්ප්රේජ ප්රේජ්ජ

3.7.516 44.738 44.037 44.037 44.037 44.037 57.137 71.137 7

183.084 185.291 185.243 185.244 185.247 187.674 189.027 189.028 190.287 190.287 191.204 193.203 193.203 194.218 195.343 195.343 195.343 195.343

211.670

213.105 213.816 214.526 215.234 215.940

216.649 217.361 218.076 218.726 219.436 220.149 222273

25.666 26.270 26.920 27.618 28.345 29.124 29.962 31.145 31

205.512 206.340 207.146 207.934 208.706

21.056 21.157 21.281 21.606 21.606 22.307 22.306 23

203.783

cocco cocco cocco cocco cocco cocco cocco cocco cocco

CURRENT: December 1983 (1 bar)

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

Enthalpy Reference Temperature = T, = 298.15 K

0.4 kJ·mol⁻¹

0.4 kJ·mol⁻¹

A_r = 39.0983 Potassium (K)

 $S^{\bullet} - [G^{\bullet} - H^{\bullet}(T_{\bullet})]T$

ئ

Σ×

60,340

20.786

NFINITE -18.284 -13.605 -10.595

log Kr

-10.499 -8.306 -6.704 -5.466 -4.481

55.652 51.335 47.086 42.894 4.652

33,594

164.419 166.147 167.816 169.404 170.905

20.786 20.786 20.786 20.786 20.786 20.786 20.786 20.786 20.786

-3.017 -1.983 -1.215 -0.625

FUGACITY = 1 bar

20825 22.904 24.983 27.064 29.147 33.322 33.321 35.415

178.351 179.384 180.369 181.313 182.217

20.814 20.836 20.868 20.914 20.975

172,323 173,662 174,929 176,129

171.476

186,300

20.786

039.540

IDEAL GAS Potassium (K)

	_
	ou.
7_	5 J·K ⁻
.02 cm	± 0.02
0.78 ± 0.02	50.340
35009.	K)= 16
(8)	8.15

$\Delta_t H^{\circ}(0 \text{ K}) = 89.9 \pm $ $\Delta_t H^{\circ}(298.15 \text{ K}) = 89.0 \pm $	
	els and Quantum Weights

•			
	Weights 8,	0040	1 . 4
	Electronic Levels and Quantum Weights State	0 12985.170 13042.876 21076.551	34991.2
	Electronic State	2Sra 2Pra 2Pya 2Sra 2Sra 2Sra 2Sra 2Sra 2Sra 2Sra 2Sr	7. 19. 19.

Enthalpy of Formation

The entialpy of formation of potassium gas, $\Delta H^0(298.15 \, \mathrm{K}) = 89.0 \pm 0.4 \, \mathrm{kl \cdot mol^{-1}}$, is chosen to be the value recommended by CODATA. This value was obtained from 2nd and 3rd law treatments of vapor pressure data. The reported vapor pressures were corrected for the effects of $K_2(g)$, using $D_0^0 = 49.01 \, \mathrm{kl \cdot mol^{-1}}$. At higher pressures an alternate virial treatment was employed. As stated by CODATA, the selected value is the weighted average of the 3rd law values of Dan H° (298.15 K) calculated from the following

Source	Δ _{sst} H°(298 15 K), kJ·mol ⁻¹	Source	Δ _{sub} H°(298.15 K), kJ·mol ⁻¹
Havcock and Lamplough ²	89.31 ± 0.65	Venogradov and Volyak ¹³	89.27 ± 0.65
Fiock and Rodenbush	89.41 ± 0.65	Achener14	88.97 ± 0.69
Edmondson and Egenton*	89.71 ± 0.25	Ahpil'rain et al. 15	88.94 ± 0.47
Weiler	89.71 ± 0.65	Bowles 16	88.50 ± 1.35
Mayer	88.58 ± 1.00	Gerasimov et al. 17	89.43 ± 0.50
Neumann and volker	89.56 ± 0.25	Sphil'rain and Nikanorov18	88.70 ± 0.85
Walling®	88.59 ± 0.75	Schins et al. 19	88.94 ± 0.50
Makansi et al.	88.73 ± 0.72	Bonilla ²⁰	88.75 ± 0.65
Buck and Pauly10	89.72 ± 0.35	Roeder and Morawitz ²¹	89.59 ± 0.38
Stone et al."	88.81 ± 0.90	Kondrat'ev ²²	88.27 ± 0.55
Rigney et al. 12	88.90 ± 0.93		

The 2nd law calculations from the above sources led to somewhat more positive values.

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatonuc gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP-kT) technique as the cutoff procedure in the energy level summation.

The atomic energy levels have been taken from the compilation of Corliss and Sugar. 14 Our calculated values for the thermal functions are ionization potentials vary from 43487.29 cm⁻¹ cm for Li to 31406.1 cm⁻¹ for Cs. In calculating the thermal functions with the inclusion of The lowest lying levels for these metals [14904 cm⁻¹ (Li), 16956 cm⁻¹ (Na), 12985 cm⁻¹ (K), 12578 cm⁻¹ (Cs)] do not contribute to the hermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the hermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 99(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.²⁴ imilar to those recommended by CODATA.1 They do differ for two reasons, however. First, the entropy differs by 0.1094 J.K.1-mol-1

198.294 198.766 199.231 199.694 200.153

200.608 201.059 201.508 201.953 202.396

References

D. Cox, chairman, CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. 10, 903 (1978).

occause this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm Second, the entropies at

98.15 K for all alkali metal gases differs by ~0.004 J·K -1 mol -1, presumably due to the use of slightly different values for auxiliary data.

T. Heycock and F. E. E. Lamplough, Proc. Chem. Soc. 28, 3 (1912). F. Fiock and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).

Continued on page 1489

Potassium (K)

PREVIOUS: June 1962 (1 atm)

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

6.355 -6.002 -5.674 -5.367

316.302 310.258 304.141 297.955 291.703

472.494 474.459 476.399 478.311 480.192

47.846 49.925 52.004 54.082 56.161

199.592 200.376 201.132 201.862 202.566

20.786 20.786 20.786 20.786 20.786

-4.809 -4.315 -4.088 -3.874

285.390 279.017 272.589 266.107 259.576

482.037 483.844 485.617 487.339 489.013

203.248 203.908 204.548 205.168 205.711

20.786 20.786 20.786 20.786 20.786

\$25,000 \$25,00

-18.761 -17.009 -15.230 -14.238 -14.238 -12.140 -11.249 -9.794 -9.794 -9.764 -9.764 -9.774 -9.764 -9.774 -9

371.845 366.768 361.569 356.255 350.832 345.305

452.064 454.139 456.211 458.279 460.342

339.682 333.965 328.160 322.271

462.398 464.445 466.480 468.502 470.508

37.453 39.532 41.610 43.689 45.768

195.153 196.120 197.044 197.928 198.777

20.786 20.786 20.786 20.786 20.786

-39.009 -32.599 -27.780 -24.024 -21.012

448.083 436.860 425.468 413.929 402.260

514.876 516.037 517.217 518.392 519.536

6274 8353 10.431 12.510

162.053 163.641 165.142

69

20.786 20.786 20.786 20.786

395.089 390.762 386.262 381.602 376.793

443.753 445.832 447.910 449.988

16.667 18 746 20.824 22.903 24.982 27.060 29.139 33.296 35.375

166.560 167.899 169.165 170.365 171.504 173.620 173.620 173.648 175.548

20.786 20.786 20.786 20.786 20.786 20.786 20.786 20.786 20.786

189.500 190.760 191.948 193.072

194.138

183.520 185.184 186.725 188.159

181.712

-84.260 -83.705 -70.926 -61.367 -53.924 -47.963

-3.671 -3.478 -3.295 -3.121 -2.125 -2.736 -2.645 -2.645 -2.645 -2.362 -2.362

119.497 205.866 198.984 192.099

497.775 498.978 500.095 501.399 502.399

209 060 209 560 210.050 210.527 210.595

20.786 20.786 20.786 20.786 20.786

239.711 233.008 226.269

490.632 492.193 493.691 495.122

173.18 178.57 179.77 181.190 1

206.356 206.926 207.480 208.020 208.546

20.786 20.786 20.786 20.786 20.786

252.997

58.239 60.318 62.397 64.475 66.554 68.632 70.711 72.790 74.868

-2.103 -1.981 -1.864 -1.752

504.155 505.016 505.680 506.253

211.451 211.898 212.336 212.765 213.185

20.786 20.786 20.786 20.786

213.596

20.786

20.786 20.786 20.786 20.786

503,312

79.025 81.104 83.183 85.261 87.340 89.418 91.497 93.576 95.654

-1.540 -1.441 -1.344 -1.162

150.398

506.731

-1.076

K;(g)

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

Enthalpy Reference Temperature = T, = 298.15 K

M, = 39.09775 Potassium, Ion (K*)

k. mol Δ_H

 $H^{\bullet}-H^{\bullet}(T_{\bullet})$

 $S^{\bullet} - [G^{\bullet} - H^{\bullet}(T_{\bullet})]T$

154.576

20.786

98.15

log Kr

δ

508.695

CURRENT: December 1983 (1 bar)

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IDEAL GAS

 $P(K^*, g) = 255100 \pm 100 \text{ cm}^{-1}$ $S^0/98 + S = 154 + 0.025 + K^{-1} + 0.001^{-1}$ S°(298.15 K)

 $\Delta_t H^{\circ}(0 \text{ K}) = 508.7 \pm 0.4 \text{ kJ·mol}^{-1}$ $H^{\circ}(798.15 \text{ K}) = 1514.0071 \text{ kJ·mol}^{-1}$

s (298.13 K) = 134.3/0 ± 0.023 J·K ·mol			Δ _t H '(298.15 K) = [514.007] KJ·mol ·
	Electronic I State	Electronic Level and Quantum Weight state	Weight 8,
	s _o	0	-
Enthalpy of Formation $\Delta H^0(K^2, g, 0, K)$ is calculated from $\Delta H^0(K, g, 0, K)$.	0 K)¹ using the	spectroscopic value	nthalpy of Formation $\Delta H^3(K, \epsilon, 0 K)^4$ using the spectroscopic value of $D(K) = 35009.78 \pm 0.02$ cm ⁻¹ (418.810 ± 0.000
kJ·mol-1) from Corliss and Sugar. The ionization which is derived from the 1973 CODATA funda	limit is converted mental constants	from cm ⁻¹ to kJ·m , Rosenstock et al	kJ·mol ⁻¹) from Corliss and Sugar ² . The ionization limit is converted from cm ⁻¹ to kJ·mol ⁻¹ using the factor, 1 cm ⁻¹ = 0.01196266 kJ·mol ⁻¹ , which is derived from the 1973 CODATA fundamental constants. Rosenstock <i>et al.</i> ⁴ and Levin and Lias ⁵ have summarized additional

 $\Delta_t H^0(K^+, g, 298.15 \, K)$ is calculated from $\Delta_t H^0(K, g, 0 \, K)$ by using IP(K) with JANAF¹ enthalpies, $H^0(0 \, K) - H^0(298.15 \, K)$, for K(g), K*(g), and e^(ref). $\Delta_t H^0(K \to K^+ + e^-, 298.15 \, K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. $^4\Delta_t H^0(298.15 \, K)$ should be changed by $-6 \, 197 \, k \, J - mol^{-1}$ if it is to be used in the ion ionization and appearance potential data.

convention that excludes the enthalpy of the electron

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar, 2 is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function 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; the first excited state is approximately 162507 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. The reported uncertainty in 5°(298 15 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.

References

²C. Corliss and J. Sugar, J. Phys. Chem. Ref. Data 8(4), 1109–1145 (1979).
³E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data 2, 663 (1973). JANAF Thermochemical Tables: K(g), 12-31-83; e (ref), 3-31-82.

⁴H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data 6, Supp 1, 783 pp. (1977).
⁴R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS-NBS-71, 634 pp. (1982).

R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F4460-75-1-0048, (1978).

Potassium, lon (K*)

PREVIOUS March 1965 (1 atm)

CURRENT December 1983 (1 bar)

M = 39 09885 Dotaesium Ion (K-)
IDEAL GAS
sjum. Ion (K ⁻)

<u>6</u> L.

Potassium, Ion (K ⁻)	IDEAL GAS	M,=39.09885 Potassium, Ion (K ⁻)	otassiun	ı, Ion (K	_					K7(9
EA(K, g) = 0.50147 \pm 0.00010 eV S°(298.15 K) = 154.577 \pm 0.005 J K ⁻¹ ·mol ⁻¹		$\Delta_t H^0(0 \text{ K}) = 41.5 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta_t H^0(298.15 \text{ K}) = [34.419] \text{ kJ} \cdot \text{mol}^{-1}$	Enthalpy Re	ference Ter	emperature	Enthalpy Reference Temperature = T, = 29&15 K		Standard State Pressure	Pressure = p	- p - 0.1 MPa
			7.K	ಚ	ر د د	-[G*-H*(T,)]/T	$H^{\bullet}-H^{\bullet}(T_i)$	Δ'Η*	Δ.6•	log Kr
1	Electronic Level and Quantum Weight State		° 2 8 8	0. 20.786 20.786 20.786	0. 131.869 146.277 150.916	INFINITE 173.057 156.478 154.919	-6.197 -4.119 -2.040	41.501		
_	1S ₀ 0.0 1		298.15	20.786	154.577	154.577		34.419	13.868	-2.430
			888	20.786 20.786	154.705	154.577	0.038	34,364	13.740	-2.392
Enthalpy of Formation. The enthalpy of formation, at 0 K, for K^g) is calculated from the adopted electron affinity, EA(K, g) = 0.50147 ± 0.00010 eV	calculated from the adopted electron affi	nity, EA(K, g) = 0.50147 ± 0.00010 eV	388	20.786 20.786 20.786	163.133 165.323	156.119 156.119 156.932	3.156	28.886 27.322 25.778	5.232 2.861	-1.016 -0.607 -0.299
(48.384 ± 0.010 kJ·mol ⁻¹). This value, recommended by Hotop and Lineberger, ⁸ was measured by a tunable laser photodetachment threshold technique. Additional discussion on K ⁻ (g) may be obtained in the critical discussions of Hotop and Lineberger, ⁸ Rosenstock <i>et al.</i> , ³ and	y Hotop and Lineberger,* was measured by rained in the critical discussions of Hotop	a tunable laser photodetachment threshold and Lineberger, 6 Rosenstock et al., 3 and	888	20.786	169.113	158.656	6274	19.743	-1.437	0.125
Massey. $\Delta_H^0(K \cdot g, 298.15 \text{ K})$ is obtained from $\Delta_H^0(K, g, 0 \text{ K})$ by using EA(K, g) with JANAF ³ enthalpies, $H^0(0 \text{ K}) - H^0(298.15 \text{ K})$, for $K^-(g)$,	JK) by using EA(K, g) with JANAF' enth	alpies, H°(0 K)-H°(298.15 K), for K ⁻ (g),	888	20.786 20.786 20.786	17.54 179.73	162.033 163.641 165.142	15.55 15.89 15.89 15.89	13.783 10.770	-8.392 -11.583 -14.241	0.501 0.672 0.744
K(g), and e (ref), $\Delta H^2(K \to K + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al. $^3 \Delta_t H^2(298.15 K)$ should be changed by +6.197 kJ·mol ⁻¹ if it is to be used in the ion convention which excludes the enthalpy of the electron.	s from a room-temperature threshold energ H"(298 15 K) should be changed by +6.1! 1.	yy due to inclusion of these enthalpies and 97 kJ·mol⁻¹ if it is to be used in the ion	200000	20.786 20.786 20.786 20.786	181.712 183.521 185.185 186.725	166.560 167.899 169.166 170.366	16 667 18.746 20.874 22.903	-71.249 -73.327 -75.406 -77.485	-11.984 -6.504 -0.851 4.961	0.283 0.283 0.034 -0.185
Heat Gapacity and Entropy The ground state configuration for K [*] (g) is given by Hotop and Lineberger ^{1,6} and Rosenstock et al. ³ Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.	Hotop and Lineberger ¹⁶ and Rosenstock of too stable excited states exist.	et al. ³ Lacking any experimental evidence	88988	20.786 20.786 20.786 20.786	189.501 190.761 191.949 193.073	172.588 173.620 174.606 175.548	27.060 29.139 31.217	-81.645 -83.728 -85.813 -87.902	23.254 23.254 29.607 36.076	-0.556 -0.715 -0.859
References If Hoon and W. C. Linsbarrer, I. Dhue, Cham. Def. I	Dots 4 \$30 (1075)		7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	20.786 20.786	195.153	176.451	35,375	-92.098	42.656	-1.114
 In noop and Tr. C. Lincockgul, J. Phys. Carlit. Ref. Data 4, 539 (1972). Slater, F. H. Read, S. E. Novick, and W. C. Lineberger, Phys. Rev. A 17, 201 (1978). H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data 6, Supp. 1, 783 pp. (1977). 	rger, Phys. Rev. A 17, 201 (1978). f. Data 6, Supp. 1, 783 pp. (1977).		7,500 7,500	20.786 20.786 20.786 20.786	197.044 197.044 198.777	178.952 179.725 180.470	41.610 43.689 45.768	-94208 -96330 -98.465 -100.617	63.005 63.005 140 141	-1.431 -1.523 -1.610
In. S. W. Maxsey, "Negative tons," 3rd ed., Cambrid, "JANAF Thermochemical Tables: K(g), 12–31–83; e ⁻¹ ⁶ H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. I	ge University Press, Cambridge, 141 pp. ((ref), 3–31–82. Data, 14, 731 (1985).	1976).	2600 2700 2800 2800	20.786 20.786 20.786	200.377 200.133	181.190 181.886 182.560	47.846 49.925 52.004	-102.787 -104.980 -107.197	84.190 91.423 98.738	-1.691 -1.769 -1.842
			3000	20.786	202.567	183.847	56.161	-111.719	113.605	-1.978
		1000	3200 3200 3400 3500	20.786 20.786 20.786 20.786 20.786	203.248 203.908 204.548 205.168	184.462 185.059 185.640 186.205	58.239 60.318 62.397 64.475	-114.030 -116.381 -118.765 -121.201	128.77 128.77 136.475 144.246	-2.041 -2.102 -2.160 -2.216
			3600	20.786	206.357	187.292	68.632 10.71	-126221	160 004	-2322 -2322
			4000 4000	20.786 20.786	208.020 208.547	188.823 189.310	74.868	-131.477 -134.204 -136.995	184.176 192.374	-2.467 -2.512
			4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	20.786 20.786 20.786 20.786	209.060 209.561 210.050 210.528 210.528	189.785 190.250 190.705 191.150	79.025 81.104 83.183 85.261 87.340	-139.865 -142.819 -145.859 -148.712 -151.869	208.984 208.984 217.396 225.852 234.401	-2556 -2599 -2641 -2681
			4460 644 600 644 644 644 644 644 644 644	20.786 20.786 20.786	211.452 211.899 212.336	192.013 192.431 192.841	89.418 91.497 93.576	-155.114 -158.428 -161.724	243.020 251.709 260.457	-2.760 -2.797 -2.834
			2000	20.786	212.765	193.244	95.654 97.733	-165.217 -168.802	269.289 278.192	-2.871 -2.906
			2300 2300 2400	20.786 20.786 20.786 20.786	213.596 214.000 214.396 214.785	194,026 194,406 194,779 195,146	99.811 101.890 103.969 106.047	-172,481 -176,254 -180,123 -184,087	287 169 296.218 305.341 314.537	-2.941 -2.976 -3.009
			5500 5600 5600	20.786	215.166	195.507	108.126	-188.145	333.154	-3.075
		***************************************	2800	20.786 20.786 20.786	216.270 216.625 216.975	196.552 196.890 197.221	114362 116.440 118.519	-200.487 -204.863 -209.320	352.015 361.579 371.217	-3.139 -3.170 -3.201 -3.232

Enthalpy of Formation

Heat Capacity and Entropy

PREVIOUS

(g) O'

CURRENT December 1967 (1 bar)

PREVIOUS: December 1967 (1 atm)

Potassium Oxide (KO)	IDEAL GAS	M _r =55.0977 Potassium Oxide (KO)	Potassium	Oxide	(KO)					Ϋ́
$S^{(298.15 \text{ K})} = [238.027 \pm 2.1] \text{ J·K}^{-1} \cdot \text{mol}^{-1}$		$\Delta_H^{\circ}(0 \text{ K}) = [72.89 \pm 41.8] \text{ kJ·mol}^{-1}$ Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$ $\Delta_H^{\circ}(298.15 \text{ K}) = [71.13 \pm 41.8] \text{ kJ·mol}^{-1}$	Enthalpy Re	ference Tea	rence Temperature = T, =	- 29&15 K		Standard State Pressure = $p^* \approx 0.1$ k1-mol ⁻¹	Pressure =	0.1
•			τÆ	ដ	$S^{*} - [G^{*} - H^{*}(T_{*})]T$	(T,)[/T	HH	$\Delta_t H^{\bullet}$	Φ_{iG}	log K
	Electronic Level and Ouantum Weight		0	0.	O. INFL	NITE	-9.666	72.886	72.886	INFIN
	State e, cm ⁻¹ g,		88	34.332	223.966 241	268.756 241.275	-5.727	72.640	57.109	-33.8

Enthalpy of Formation

Brewer and Margrave¹ suggested that the Δ_H^0 value for MO(g) from the gaseous ions can be taken as the mean of the corresponding Δ_H^{0} values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal·mol⁻¹. We obtain the values $\Delta_H^{0}(0 \, K) = -137.94$ and -117.7 kcal·mol⁻¹ for the reactions $K^{\circ}(g) + F^{\circ}(g) = KF(g)$ and $K^{\circ}(g) + Cl^{\circ}(g) = KCl(g)$, respectively. Assuming $\Delta_H^{0}(0 \, K) = -127.83$ kcal·mol⁻¹ for the reaction $K^{\circ}(g) + O^{\circ}(g) = KO(g)$, we calculate $\Delta_H^{0}(KO, g, 298.15 \, K) = 19.0$ kcal·mol⁻¹ with the JANAF auxiliary values for the gaseous ions.

r. = [2.2] Å **d =** 1

 $\alpha_e = [0.0027] \text{ cm}^{-1}$ ωεχ = [2.2] cm⁻¹

ω_e = [350] cm⁻¹ B_e = [0.3068] cm⁻¹

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0

[H₂]

Based on the assumption that $D_0^2(KO) = 1/2[D_0^2(K_2) + D_0^2(D_2)]$, or $\Delta_1 H^0(0|K) = 64.9$ kcal mol⁻¹ for the reaction KO(g) = K(g) + O(g), we

evaluate $\Delta_t H^{\circ}(KO, g, 0 K) = 15.6 \text{ kcal-mol}^{-1} \text{ or } \Delta_t H^{\circ}(KO, g, 298.15 K) = 15.2 \text{ kcal-mol}^{-1}.$ According to Somayajulu, ² in a sequence of similar diatomic molecules, $L_F L^{\circ}D_0^{\circ} = \text{constant}$, where $L_F L^{\circ} L$ frequency for the diatomic molecule and μ is the reduced mass.

The value of $\Delta H^{*}(KO, g, 298.15 \text{ K})$ is tentatively adopted as $17 \pm 10 \text{ kcal mol}^{-1}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for the OH(g) molecule, which has the same number of valence electrons. The values of ω, and ω, ε, are estimated by comparison with those for LiF(g) and KF(g). The bond distance is estimated from those for HO(g), HF(g) and KF(g). Be and αe are derived from re, ωe and ωεχe by the method suggested by Herzberg.

References

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 Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

-49.535 -39.613 -29.595 -19.486 -9.289 0.995 11.362 21.811 32.340

-275.554 -277.800 -280.071 -282.372 -284.704

39.788 39.883 39.977 40.071

42.947 53.631 64.390 75.224 86.132

-291.915 -294.403 -296.938 -299.527

88.682 92.666 96.659 100.661 100.673 100.673 116.764 112.725 116.764 120.814 123.940 133.017 141.199 141.199

315.545 316.825 318.068 319.277 320.453

40.258 40.352 40.445 40.538

280.482 281.598 282.685 283.743 284.775 285.765 286.765 286.765 286.765 288.665

321.599 322.716 323.806 324.870 325.909

40.725 40.818 40.911 41.004

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-307.648

153.104 164.518 176.004 187.535 199.158

-313.389 -316.378 -319.451 322,334

149.419 153.542 157.675 161.817 165.969

290.481 291.361 292.222 293.067

326.925 327.919 328.891

41.190 41.283 41.468 41.468

329.843 330.776

22,619 24,444

328.784 -338.938 -342.534

170.130 174.300 178.479 182.667

331.691 332.588 333.467 334.331 335.179

11.932

294.706 295.503 296.284 297.806 298.547 299.276 299.992 300.696 301.389

336.012 336.831 337.636 338.428 339.206

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238.582 260.467 260.467 260.470 260.457 260.260 271.686 271.68

305,329 306,948 308.506 310.010 311.462 312.866 314.226

-78.697 -69.082 -59.360

49.373 53.260 57.157 64.980 68.907 72.843 76.788 80.743

300.061

39.312 39.408 39.504 39.599

38.820 38.921 39.020 39.118

-253.957 -256.076 -258.201 -260.331 -262.469

-150.962 -142.465 -133.792 -124.957 -115.971

-243.418 -245.516 -247.620 -249.728

252.357 254.535 256.608

281.413 284.271 286.938 289.440 294.024 296.137 298.145

38.279 38.395 38.506 38.614 38.718

-149517 -152,460 -155,405 -158,375 -161,388

11.132 14.890 18.669 22.464 26.277 30.094 33.928 33.773 41.629 45.496

247.641

71.357 275,000

37.473 37.693 37.870 38.021 38.155

-141*987* -143*533* -145*0*52 -146*5*52

226.308

226.308

35.888

-106.844

67 (1 bar)

-3.095 -3.154 -3.213 -3.271

246.353 258.334 270.388 282.515 294.716 306.990 319.339

K,07(g)

Standard State Pressure = p = 0.1 MPa

log Kr

ģ

 $H^{\bullet}-H^{\bullet}(T_i)$

 $-[G^{\bullet}-H^{\bullet}(T_t)]T$

ž

-130.087 $\Delta_i H^{ullet}$

Potassium Oxide, Ion (KO⁻)

IDEAL GAS

M_r = 55.09825 Potassium Oxide, Ion (KO⁻)

Enthalpy Reference Temperature = T, = 298.15 K

[·K-'mol-'-

 $\Delta_t H^{\circ}(0 \text{ K}) = [-130.09 \pm 83.7] \text{ kJ·mol}^{-1}$ $\Delta_t H^{\circ}(298.15 \text{ K}) = [-138.07 \pm 83.7] \text{ kJ·mol}^{-1}$

 $S^{(298.15 \text{ K})} = [226.308 \pm 1.3] \text{ J-K}^{-1} \cdot \text{mol}^{-1}$

Potassium Oxide, Ion (KO⁻)

r. = [2.2] A 1 = 0 Ξ Electronic Level and Ouantum Weight α_c = [0.0027] cm⁻¹ ωξ. = [2.3] cm⁻¹ £. GB.1 0 State M $\omega_c = [360] \text{ cm}^{-1}$ $B_c = [0.3068] \text{ cm}^{-1}$

Enthalpy of Formation

Since the electron affinity of KO(g) is unavailable, the value of $\Delta H^0(KO^-, g, 298.15 \, K)$ is estimated. Assuming that the enthalpy change $\Delta H^0(0 \, K)$ of the reaction (1) KO⁻(g) = K(g) + O⁻(g) is approximately the average of the $\Delta H^0(0 \, K)$ value for the reaction (2) KO(g) = K(g) + O(g) and (3) KF(g) = K(g) + F(g), we obtain $\Delta H^0(0 \, K) = 1/2(63.5 + 117.3) = 90.4 \, kcal \, mol^{-1}$ for reaction (1). However, we compare the AH'(0K) values for the reactions (4) HO(g) = H(g) + O(g), (5) HO^(g) = H(g) + O^(g), and (6) HF(g) = H(g) + F(g), and find of $\Delta_H^{*}(0 \text{ K})$ values for reactions (4) and (6). Based on this fact we estimated $\Delta_H^{*}(0 \text{ K}) = 80 \text{ kcal} \cdot \text{mol}^{-1}$ for reaction (1), yielding $\Delta_H^{*}(\text{KO}_{-})$, $\epsilon_{\mu} = 298.15 \text{ K}) = -33 \text{ kcal} \cdot \text{mol}^{-1}$. The value of $\Delta_H^{*}(\text{KO}_{-})$, $\epsilon_{\mu} = 298.15 \text{ K}$ is tentatively adopted as $-33 \pm 20 \text{ kcal} \cdot \text{mol}^{-1}$. The electronic affinity of KO(g) is derived to be 2.2 ± 0.9 eV. The value of EA for HO(g) is determined as 1.8 ± 0.1 eV. that AH 70 K) for reaction (5) is experimentally determined as 109.7 kcal-mol-1 which is about 8 kcal-mol-1 more negative than the average

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of KF(g) which is isoelectronic with KO [g). The values of ω_{κ} , ω_{κ} , and r_{κ} are estimated by comparison with those for KF(g). The values of B_{κ} and ω_{κ} are eactulated from r_{κ} , ω_{κ} and ω_{κ} , using the method recommended by Herzberg

'G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, (1950). Reference

<u> </u>	CURRENT: Decemb	CUR			1967 (1 atm)	December	PREVIOUS:
	382.137	-383.082	229.353	304.698	342.923	42.950	0009
	369.421	-378.622	225.062	304.056	342,202	42.858	2900
•	356.780	-374245	220.781	303,404	341.470	42.765	2800
•	344,213	-369.954	216.509	302,743	340.727	42.673	5700
	331.763	-366.054	212.247	302.071	339.973	42.580	2000

Standard State Pressure = p° = 0.1 MPs

 $H^{\bullet}-H^{\bullet}(T_t)$

 $S^{\bullet} - [G^{\bullet} - H^{\bullet}(T_{\bullet})]T$

188 849 129.436

0. 46.225 92.567 22.499

0. 52.400 69.454

122.499

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298 15

NFINITE 141.753 66.699 log Kr

> -285 480 -271.377 -255.381 -240589 -240.316

41.843 29.440 22.029 17.134 11.103 9.126 7.562 6.077 4.724 4.724 3.552 2.633 1.811

-196.810 -183.217 -170.041 -157.237 -144.765

-276.854 -273.908 -270.921 -267.939

-225.443 -210.868

284.831

146.226 165.373

0.144 8.240 16.827 25.724 34.833 44.092 53.467

138.714 145.864 152.872 159.620 166.067

181.588 195.625 207.987 219.028 228.992

888 85888 558888

77.613 83.889 87.655 90.165 91.922 94.224 94.224

-284.512 -284.478 -279.712 -127.980

-343.951 -340.021

-89.388 -70.557 -52.006

-336.097 -332.182 -328.284

72.440 81.997 91.583 101.191

172.206 178.045 183.600 188.890 193.932

238.061 246.376 254.049 261.169 267.806

95.395 95.730 95.981 96.148

Enthalpy Reference Temperature = T, = 298.15 K

K,02(cr)

 $\Delta_t H^{\circ}(0 \text{ K}) = -285.48 \pm 21 \text{ kJ-mol}^{-1}$ $\Delta_{\rm r}H^{\circ}(298.15~{\rm K}) = -284.51 \pm 2.1~{\rm kJ \cdot mol^{-1}}$ $\Delta_{\rm tri}H^{\circ} = 0.302~{\rm kJ \cdot mol^{-1}}$ Δ_{m2}H° = 0.157 kJ·mol⁻¹ $\Delta_{fus}H^{\circ} = Unknown$ S"(298.15 K) = 122.499 ± 4.2 J·K⁻¹·mol⁻¹ $T_{\rm fus} = 782 \pm 20 \, \rm K$ rui = 193.5 K r_{tr2} = 230.9 K

Potassium Superoxide (KO₂)

also measured the enthalpy of solution as -13.2 ± 0.8 kcal mol⁻¹ from which we obtain $\Delta_t H^0(\text{KO}_2$, cr. 298.15 K) = -67.88 ± 0.8 kcal mol⁻¹ Both $\Delta_t H^0(\text{KO}_2$, cr. 298.15 K) = -68.0 ± 0.5 Δ_tH*(KOHaq, 12,000 H₂O, 298 15 K) = -115.243 kcal·mol^{-1 2} and Δ_tH*(H₂O, 1, 298 15 K) = -68 315 kcal mol^{-1 3} Giles and Margrave* D'Orazio and Wood" measured the enthalpy of solution, Δ_{ab} H°(25°C) = -13.0 ± 0.4 kcal mol⁻¹ for KO₂(xr) + 1/2 H₂O(t). KOH(aq, 2,000 H₂O) + 3/4 O₂g) which leads to $\Delta H^{\circ}(KO_2, cr, 298 15 K) = -68.09 \pm 0.4$ kcal-mol⁻¹, using the following auxiliary data. kcal·mol-1 is adopted in the tabulation. Enthalpy of Formation

Kazamovskaya and Kazamovskii² and deForcrand⁸ determined the enthalpy of solution in H₂SO₄(a₁) and derived the heat of formation of KO₂(c₁) as -67.9 kcal mol⁻¹ and -66.8 kcal·mol⁻¹, respectively. The former is reliable since their sample was well characterized and corrections for the impurities were included in the $\Delta_{ab}H^{\circ}$ data. The latter did not give enough experimental details to check their derivation.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range from 52 298 K are obtained from Todd's measurements. Two peaks at 193.5 K and 230.9 K were found in his heat capacity data. Below 50 K, the heat capacities were extrapolated using a combination of 1 Debye cal-K-1 mol-1 at 50 K. By neutron diffraction, Smith et al. found an antiferromagnetic transition at 7 K which indicates the existence of an (9 = 139) and 2 Einstein (9 = 260) functions as suggested by Todd. This extrapolation yields the entropy from lattice contribution as 3.278 unpaired electron in KO₂(cr). We tentatively adopt 5°(50 K) = 4.656 ± 1 cal·K⁻¹·mol⁻¹ which includes both lattice (3.278 cal·K⁻¹·mol⁻¹· and unpaired electron (Rln2) contributions. Heat capacities above 298 K are estimated graphically.

The entropy at 298 K is calculated from the C, data and is based on an extrapolation of S'(50 K) = 4656 cal·K⁻¹·mol⁻¹.

Transition Data

Todd observed two anomalies in the heat capacity at 193.5 and 230.9 K which are adopted as two phase transitions in the tabulation. The heats of transition are calculated from the total heats of absorption given by Todd between 180 and 208 K for transition 1 and 217-240 K for transition 2 with extrapolated C, below 176 K and above 250 K.

Smith et al * confirmed these two transitions in the neutron diffraction measurements. In addition, they found an antiferromagnetic transition at 7.1 ± 0.5 K and an unusually low temperature phase transition at 12 K Neuman8 observed a color change at 75.7 ± 15°C in the warning and cooling curves for KO_ACr). Thus color change represents a phase transition which is in good agreement with Todd's observation

Fusion Data

Firsova et al. 10 studied the thermograms of KO₂(cr) and found the melting point 509 ± 20°C under atmospheric pressure which is adopted in the tabulation. Earlier melting point data were reported as 380°C by Bluemental" and 440°C by deForcrand.

References

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²This value is derived from JANAF $\Delta_t H^0$ (KOH, aq, ∞ , 298.15 K) = -115.273 kcal·mol⁻¹ with the heat of dilution data from V. B. Parker, NSRDS-NBS 2, (1965)

³U. S. Nat. Bur. Stand. Tech. Note 270-3, (1968).

⁴P W. Gilles and J. L. Margrave, J. Phys. Chem. 60, 1333 (1956).

⁵L. I. Kazamovskaya and I. A. Kazamovskii, Zh. Fiz. Khim. 25, 293 (1951)

⁶M. R. deForcrand, Comp. Rend. 158, 843 (1914).

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PREVIOUS: June 1962

Potassium Superoxide (KO₂)

CURRENT. June 1971

K₁O₂(cr)

| §

CURRENT: December 1983 (1 bar)

PREVIOUS: June 1962 (1 atm)

Potassium (K₂)

 $M_r = 78.1966$ Potassium (K₂)

 $D_0^0 = 53.48 \pm 1.20 \text{ kJ·mol}^{-1}$ (natural abundance) S°(298.15 K) = 249.690 \pm 0.042 J·K⁻¹·mol⁻¹

IDEAL GAS

Potassium (K₂)

 $\Delta_t H^{\circ}(0 \text{ K}) = 127.11 \pm 2.0 \text{ kJ}$ $\Delta_t H^{\circ}(298.15 \text{ K}) = 123.68 \pm 2.0 \text{ kJ}$

$^1\Sigma_g^+$) in cm $^{-1}$	ω _{3/ε} = -2.055 × 10
Spectroscopic Data for 39K2 (Ground State. 1\(\Sigma_{\beta}\)) in cm ⁻¹	$\omega_{\rm e} \zeta_{\rm e} = 0.2829$ $\alpha_{\rm e} = 1.65 \times 10^{-4}$ (a) $r_{\rm e} = 3.9051 \text{ Å}$
Spectrosc	$\omega_{\rm c} = 92.021$ $B_{\rm c} = 0.056743$ $D_{\rm c} = 8.63 \times 10^{-8}$

Enthalpy of Formation

(a) -7.2×10^{-6} (v + 1/2)² + 1.5 × 10⁻⁷ (v + 1/2).³

Using the adopted value of the dissociation energy for natural abundance $K_2(g)$, $D_0^0 = 53.477$ kJ·mol⁻¹ [D_0^0 for $^{39}K_2 = 53.474$ kJ·mo determined by Tango *et al.*?], and the recommended $\Delta_H^{a}(K, g, 0 K) = 90.14$ kJ mol⁻¹ from NBS,* we calculate $\Delta_H^{a}(K_2, g, 0 K) = 1$ kJ·mol⁻¹. Since this value is only 0.31 kJ·mol⁻¹ smaller than the NBS recommended value of 127.1 kJ·mol⁻¹, we adopt the NBS Correcting this value to 298.15 K using the current $H^0(298.15 \text{ K}) - H^0(0 \text{ K}) = 1.0738 \text{ kJ·mol}^{-1}$ for K₂(g) and the NBS value of $H^0(298.15 \text{ K}) - 1.0738 \text{ kJ·mol}^{-1}$ for K(cr),* we obtain $\Delta_H^{a}(K_2, g, 298.15 \text{ K}) = 123.68 \text{ kJ·mol}^{-1}$.

Heat Capacity and Entropy

were calculated from the "kf.(g) data using mass reduced scaling. The rotational levels were weighted according to the nuclear spins individual atoms ("kk, 1–3/2, "lk, 1–4) as follows: "kk, even J weight = 0.625, odd J weight = 0.375, "ks, even J weight = 0.556, weight = 0.444. The adopted value of \$^(298 15 k) is only 0.15 J·K⁻¹-mol⁻¹ lower than that adopted by NBS. The heat capacity and entropy were calculated using a direct summation technique similar to the Li₂(g) species (see Li₂(g) table) usingiven above. ¹³ Since insufficient spectroscopic data exist for the lower lying excited electronic states, weperformed the calculation ground state only. Based on the results of Li, and Na,, we expect that the neglect of these excited states results in only ca. 1-2% low only 1.3 J·K⁻¹ less than that calculated including the excited states). Separate calculations were performed on the isotopic species 9 K and 3 K and the results combined according to the natural atomic isotopic abundances^{1, 29}K, 93.258%; 4 K, 6 730% (the diatomic: these effects will not manifest themselves at temperatures less than ca. 3000 K (for Na4g) the entropy of the ground state only at 30 ⁴⁰K₂ was neglected due to the small isotopic abundance of 011%) The spectroscopic input data for the calculation of the isotopic energy functions near 6000 K. The heat capacity, however, above 2000 K will be senously deficient. The actual C, will probably temperature dependence similar to that calculated for Li2 and Na2. Likewise, the actual entropy will be somewhat larger than given

C. Stwalley, Director Iowa Laser Facility and Professor of Chemistry and Physics, University of Iowa, personal communication, ¹W. C. Stwalley, Director Iowa Laser Facility and Protessor of Chembay a ³W. J. Tango, J. K. Link and R. N. Zare, J. Chem. Phys. 49, 4264 (1968).

Pure Appl Chem. 47, 75 (1976).

D. D. Wagman, et al., J. Phys. Chem. Ref. Data 11, Supp. 2 (1982)

J -−lom-D	Enthalpy F	Reference T	emperature	Enthalpy Reference Temperature = T, = 298.15 K		Standard State Pressure	1 .	p = 0.1 MPa
J-Iom-D						LJ·mol-1		
	7 ¥	ಚ	ار د	-[G*-H*(T,)]T	$H^{\bullet}-H^{\bullet}(T_t)$	$\Delta_{r}H^{\bullet}$	₽ C•	log K,
	۰ <u>۵</u>	0. 36.488	0.	INFINITE 283,115	-10.738 -7.420	127.110	127.110	INFINITE - 59.125
	200	37.533	234.619	253.150	-3.706	125.488	99.961	-26.107
	298.15	37.962	249.690	249.690	o.	123.683	87.801	-15.382
	2 8	38.347	249.925	249.691	3.886	12.64	87.579 76.804	-15.249 -10.030
	8 8	38.698	269.496	254.018	7.739	114.141	67.157	-7.016
	88	38.769	282.563	260.411	15.507	109.838	57.968 49.139	-3.667
	88	38.242	287.710	263.509	19.361	107 738	40.611	-2652
nol ⁻¹ as	88	36.23	296.046	269.222	26.824	103.211	24,350	-1.878
126.80	825	34.982	299 441	271.817	30,386	-57.265	25.795	-1.225
S result.	8.8	32.482	305.079	276.519	37 129	-58.837	41.024	 5
-(NCIS	50 50 50 50	31.337	307 444 309.570	278.644 280.637	40.319	-59.805	48.742	-1.819
	160	29.352	311.494	282.506	46.381	-62.064	64.397	-2.102
	002	28.514	313.248	284.264	49.274	-63,336	72,339	-2223
ing data	865	27.114	316.340	287.482	54.831	-66 127	88.456	-2432
Wer free	2100	26.020	318 998	290,360	60 140	90.09-	10000	-2600
exhibit	2200	25.566	320 197	291.689	62.718	-70.851	113.211	-2688
here but	2400	24.804	321.325	292.953	65.254	-72.559	121.616	-2.762
200 K 15	2500	24.485	323.394	295.307	70.217	171 97-	138.651	-2.897
K2, 4 K2,	2600	24 199	324.348	296 406	72.651	-78.078	147.282	-2.959
species	380 780 780 780 780 780 780 780 780 780 7	23.715	326 124	298.466	71.440	-82.107	153.786	-3.018
species	3000	23.508	326.952 327.746	299.434 300.365	79.801 82.143	-84.237	173.621	-3.127 -3.178
6, odd J	3100	23.153	328.508	301.261	84 466	-88.749	191.553	-3.228
	3200	22 88	329.240	302 124	86.774	-91.142	200 633	-3.275
	3400	22.733	330.626	303.760	91346	-96209	219.021	-3365
(001)	9696	10.27	331 010	305 300	95.015	108,801	165.822	-3.408
.(1962).	3700	22 412	332.535	306.017		-101.727	247 189	-3.490
	98 88 38 88 38 88 38 88	22.240	333 131	306.723	100.352	-107.755	256.740	-3.529
	4000	22.163	334,272	308.072	104.801	-114344	276.091	-3 605
	4200	22.092	334.818	308 718	107.013	-117.870	285.896	-3.642
	4300	21,966	335.868	309.956	111.419	-125.452	305.769	-3.714
	\$ 2 4	21.909	336.864	311.130	113.612	-128.965 -133.091	315.791 325.944	-3.749
	4600	21.807	337.343	311.695		-137.397	336.192	-3.818
	8,00	21.718	338.270	312.783		-141.84/ -146.267	356.944	-3.884
	600 000 000 000	21.677	338.717	313,308	124.506	-151.081 -156.086	378 110	-3.917
	2100	21.604	339.583	314.321		-161.281	388.847	-3.983
	200	21.571	340.002	314.811		- 166.670	399.684	-4.015
•	888	21.510	340815	315.759	135.301	78.027	421.681	-4.079
	9000	204.12	241.205	316.218		-183,994	452.841	1.4-
	5700	21.431	341.976	317.109	141.741	-195.805	455,399	-4.142
	2800 2000 2000	21.407	342.348	317.541		-202245	466.878	-4.205
	0009	21.364	343.073	318,380		-215.634	490.178	-4267

K₂O₁(cr)

M_r = 94.1960 Potassium Oxide (K₂O)

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Potassium Oxide (K₂O)

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Δ_{e}^{1} (U.K.) = Unknown Δ_{e}^{1} (1.K.) = Unknown Δ_{e}^{1} (1.K.) = Δ_{e}^{1} (runapy K	elerence 1e	.mperature J·K ⁻¹ mol ⁻¹ .	Emilapy Keierence Temperature = I, = 29%15 K		Standard State Pressure = p = 0.1 MPa kJ·moi ⁻¹	Pressure = p	- 0.1 MPa
Enthalpy of Formation	7/K	ដ	-[C	$-[G^{\bullet}-H^{\circ}(T_{*})]T$	$H^{\bullet}-H^{\bullet}(T_i)$	$\Delta_{r}H^{\bullet}$	Δ_{iG}	log Kr
$\Delta_t H^2(298.15 \text{ K})$ was reported by Rengade ¹ based on the measurements of the enthalpy of solution of K(cr) and K ₂ O(cr) in H ₂ O. The same value of $\Delta_t H^2(298.15 \text{ K})$ was also given by de Forcrand. ²	0 0 0 0 0							
Heat Capacity and Entropy Both C. and S'008 ISK) were estimated by comparison with those of the Na. Overs	238.15	83,680	94.140	94.140		-363.171	-322.094	56.429
Decemberities Date	888	91.546 94.266	119.958	97.539 104.161	8.968 18.255	-366.782 -365.782 -365.240	-321.839 -307.331 -292.638	30.037 30.572
$T_{d,m} = 1154 \text{ K}(600\text{mmHg})$ was taken from NRC Bulletin. ³	86	97.404 101.384	158 126 173.439	111.736		-363.320 -361.000	-278.292	24.227
References	888	105.395 109.455 113.512	187.239 199.887 211.629	127.099 134.494 141.627	58.854 70.007	-358.283 -355.209 -351.817	-237.394	13.778
m. Kengate, Ann. Culm. et phys. [6] 14, 340 (1908). 2R. de Fortzand, Compt. rend. 158, 991 (1914). 3. "Data on Chemicals for Cremic Hee." National Research Council Bulletin 118 (1900).	2002	117.549	222.637	148.496		-506.056	-202.704	9.626
ACCULATION OF THE PROPERTY OF	2008	129.699	252.390 261 477	167 647 173.601		-486.816 -479.623	-122.306 -96.519	4.563 3.361
	922	137.833	270.240	179.369		-472.038 -464.062	-71,223 -46,415	2.325
	2000	150.083	294.948 302.751	195.696 200.854		-455.595 -446.939 -437.796	- 22.087 1 766 25 147	0.041 0.049 0.049
						2000	1	CO.O.
	PREVIOUS:						CURRE	CURRENT: June 1963

Potassium Oxide (K₂O)

Fusion Data

 $T_{tus} = 763 \text{ K}$

References

K203S1,(cr)

CURRENT: June 1972

M_r = 154.2803 Potassium Silicate (K₂SiO₃)

Potassium Silicate (K₂SiO₃)

 $\Delta_{\rm r}H^{\circ}(298.15 \, \rm K) = -1548.08 \pm 8.4 \, \rm kJ \cdot mol^{-1}$ $\Delta_{\rm tur}H^{\circ} = [50.208 \pm 12.6] \, \rm kJ \cdot mol^{-1}$ Hatton *et al* 'conducted enthalpy of solution measurements on K,SiO₃(cr) and KOH(cr) in HF(aq) at 50°C to determine the enthalpy of formation of the silicate. The results of this work gave a $\Delta_4 H^3(298.15 \, K) = -17.5 \pm 0.5$ kcal mol⁻¹ for the process 2 KOH(cr) + SiO₂(cr, quartz) \rightarrow K₂SiO₃(cr) + H₂O(1) When combined with the auxiliary data for H₂O(1) KOH(cr) and SiO₂(cr), ²³ we calculate $\Delta_4 H^3(K_2S_1O_3, cr, quartz)$ $S^{\circ}(298.15 \text{ K}) = 146.147 \pm 0.8 \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ 298 15 K) = -369.9 ± 1 kcal·mol-Enthalpy of Formation Fin = 1249 K

Urusov* summarized the various methods of estimating the enthalpies of formation of silicates using the Born Haber cycle and energies of atomization. His estimate for $\Delta_l H^0(K_2SlO_3, cr, 298 \ l5 \ K)$ is $-369 \ kcal \cdot mol^-$

An earlier estimate by Wilcox and Bromley' based upon ionic contributions to crystal lattice energies gave AHP(K2SiO), cr, An attempt to calculate the $\Delta_H^o(K_2SiO_3, cr, 298.15~K)$ from HF solution experiments on higher potassium silicates (K₂Si₂O₃, K₂Si₃O₃) and 298.15 K) = -367 ± 15 kcal·mol⁻¹

sodium silicates yielded a value of -383.8 kcal mol-1 which is discrepant with the former values. A value for $\Delta H^{*}(K_2SiO_1, cr, 298.15 \text{ K}) = -370 \pm 2 \text{ kcal·mol}^{-1}$ has been selected

Heat Capacity and Entropy

The low temperature heat capacity of K,SiO₃(cr) has been measured and reported by Stull *et al* ¹ in the range 15 298 K. They report S°(298.15 K) = 34.93 cal·K⁻¹ mol⁻¹ which is derived from C_p and an extrapolation of S°(15 K) = 0.18 cal k⁻¹ mol⁻¹. Heat capacities above 298 15 K have been estimated by analogy with other alkali metal silicates and borates.

Fusion Data

A melting temperature of 1249 K for K₂StO, was measured by Morey and Bowen. The enthalpy of fusion, $\Delta_{tu}H^0 = 12 \pm 3 \text{ kcal·mol-1}$, was estimated by comparison with other silicates.

W. E. Hatton, D. L. Hildenbrand, G C. Sinke and D R. Stull, unpublished data, The Dow Chemical Company, Midland, MI (1959). ²U. S. Nat Bur. Stand. Tech. Note 270-3, (1968).

¹JANAF Themochemical Tables KOH(σ), 12–31–70, SiO₂(σ), 6–30–67.

V. S. Unisov, Geoklinniya, No. 5, 551 (1965).
D. E. Wilcox and L. A. Bromley, Ind. Eng. Chem. 55, No. 7, 32 (1963).
G. W. Morey, Geophysical Laboratory, Carnegue Institute of Washington, Paper No. 1215 (1952–1953).
D. R. Stull, D. L. Hildenbrand, F. L. Oetting and G. C. Sinke, J. Chem. Eng. Data 15, 15 (1970).
G. W. Morey and H. L. Bowen, J. Phys. Chem. 28, 1167 (1924).

Standard State Pressure = p = 0.1 MPa NFINITE 791.827 388.100 118.310 99.054 84.640 73.455 64.529 56.807 50.132 253.366 185.858 145.312 44.505 39.700 35.552 31.937 28.747 25.850 23.269 20.957 18.874 16.989 255.038 <--> - 1455.160 - 1423.255 - 1390.957 -1358.985 -1377.426 -1296.307 -1265.627 -1235.369 - 1107.622 - 1064.047 - 1020.940 -1539.542 -1515 904 -1485 986 -1196.287 -1151.692 -978.278 -935.594 -890.795 -846.400 -802.399 -758.780 -715.531 -1455.733-- CRYSTAL -1548 089 -1552.872 -1551.745 -1677.256 -1670.768 -1664.155 -1657.416 -1700.727 -1693.505 -1686.116 -1678.564 -1539.542 -1544.710 -1547.151 -1539.816 -1689,825 -1683,623 -1548.080 -1549.626 -1543.488 -1535.919 -1670.852 -1662.982 -1546.808 LJ.mol- $H^{\bullet}-H^{\bullet}(T_t)$ 0219 12.971 27.172 42.492 58.632 75.420 92.728 110.455 128.505 146.887 165.526 184.375 203.434 155.996 222.701 242.177 261.863 281.758 301.862 Enthalpy Reference Temperature = T, = 29&15 K S -[C-H'(T,)]T 146.149 151.021 160.743 172.173 184.099 195.992 207.617 218.867 229.700 240.110 250.106 259.705 268.927 245.059 277.795 286.333 294.562 302.504 310.179 J-K-1mol-1 146.147 310.648 369.955 391 401 404 404 549 242.994 267.859 290.268 346.523 362.515 146.881 215 101 416.983 118 758 135.562 148.114 157.737 164.850 170 707 175.310 179 075 182 004 185 351 187.443 189.535 191.627 193.719 118.407 86 376 195.811 197.903 199.995 202.087 ئ 400 500 600 700 800 800 1100 1200 1249 000 1 298 15 8 868 $\Delta_t H^{\circ}(0 \text{ K}) = -1539.54 \pm 8.4 \text{ kJ} \cdot \text{mol}^{-1}$

Potassium Silicate (K₂SiO₃)

PREVIOUS

_
(K ₂ SiO ₃)
Silicate (
sium S
Potas
M _r = 154.2803 Po
M,= 15
LIQUID
m Silicate (K ₂ SiO ₃)

K2O3Si1(I)

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Potassium Silicate (K ₂ SiO ₃)	$S^{\circ}(298.15 \text{ K}) = [184.256] \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ $T_{\text{ta}} = 1249 \text{ K}$

Enthalpy of Formation $\Delta H^{2}(S_{2}S_{1})$, 1, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{lab}H^{2}$, and the difference in en $H^{2}(1249 \text{ K})-H^{2}(298.15 \text{ K})$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of K,SiO₃(I) has been estimated. A constant C^og of 43 cal·K⁻¹·mol⁻¹ for K,SiO₃(I) was selected above a hypothetics transition temperature of 700 K. Below this temperature the heat capacity was taken as that of the crystal S°(K,SiO₃, I, 298.15 K) is calt in a manner analogous to that used for the enthalpy of formation.

Refer to the crystal table for details.

Δ _t H*(298.15 K) = [-1499.290] kJ·mol ⁻¹	Enthalpy R	eference To	emperature	Enthalpy Reference Temperature = Tr = 298.15 K	 	Standard St.	Standard State Pressure = p = 0.1 MPa	0.1 MPa
1001.CX [0:71 = 007:0c]	ΤÆ	l U	. D]S	-[G*-H'(T,)]/T	H*-H*(T,)		Δ.6.	log Kr
ion, $\Delta_{n\nu}H^{\circ}$, and the difference in enthalpy,	0 00 0							
	300	118.407	184.256	184.256 184.259	0.	-1499.291	-1418.306	248.481
b,(l) was selected above a hypothetical glass rystal 5°(K,51O ₁ , 1, 298.15 K) is calculated	8 8	135.562	221.557 253.210	189.130 198.852	12.971 27.179	-1504 082 -1502.956	-1389.709 -1361.222	181.477 142.206
	966		281.103 305.985	210.282 222.209	42.492 58.643	-1500.837 -1498.008	-1333.061 -1305.314	116.053 97.404
	700 000 700.000		305.985 305.985	222.209 222.209	58.643 58.643	GLASS		
	888	179.912	330.008	234.216 246.060	76 634 94 625	-1493.485 -1489.129	-1278.097 -1251.437	83.451
	8 2 2	179 912	387.302	268.568	130,607	-1638.934 -1633.934	-1225.251	56.520 56.520
	1249.000		410.154	284.121	157.414	CRYST	CRYSTAL <> LIQUID	QID
	1300 1400 200 200	179.912	430.690	289.211 298.846 308.055	184581	-1627 403 -1621 773 -1616 773	- 1109.670 - 1070.056 - 1030.843	44.587 39 924 35 807
	002	179.912	454.714	316.862	220.563	-1610.764	-991 994	32.385
	0081	179.912	475 905	333.379 341.139	256.546	-1650 032 -1644,548	-911.875 -871.016	26.462 23.946
	2000	179.912	494.860	348.5%	292.528	-1639,109	-830.445	21.689
	7550 7300 7300	179.912	\$12.008 \$20.005	362.685	328.511	-1628.380 -1628.380 -1623.098	-750.098	17.810
	2400 2500	179.912	527.662 535.006	375.790 382.013	364.493	-1617.876 -1612.720	-670.721 -631.363	14.598
	2600	179 912	542.063	388.034	400.475	-1607.634	-592.209	11.898
	2800 2800 2800	179.912 179.912	548.853 555.396 561.709	393.865 399.518 405.002	418.467 436.458 454.449	-1602,623 -1597,692 -1597,847	-553.249 -514.474 -475.874	10.703 9.598 8.571
	3000	179.912	567.808	410.328	472.440	-1588.095	-437.438	7.616
	PDEVIOUS.						i E	Con contraction of
-	rhevidos.						CUKKE	101 June 1977

K₂O₃Si₁(cr,l)

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Potassium Silicate (K₂SiO₃)

(K ₂ SiO ₃)
Silicate
Potassium
$M_r = 154.2803$

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Potassium Silicate (K₂SiO₃)

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	T awar and	J·K-'mol-'	J.K. 'mol'	4	Standard St.	Standard State Pressure = p* k f.mol ⁻¹	o" = 0.1 MPa
7./	ះ	S -{G	-[G*-H*(T,)]/T	$H^{\bullet}-H^{\bullet}(T_{r})$	Ì	₽ C•	log K,
٥	0.	0	INFINITE	-21.870	-1539,542	-1539,542	INFINITE
38	98 198	103.052	236.438	- 18.949	-1544.710	-1515.904	791.827
298.15	118.407	146.147	146 147	(0.01	-1547.151	-1465.980	388.100
300	118.758	146.881	146 149	9.0	1549,090	1455.155	253,038
9	135.562	183 448	151.021	12.971	-1552.872	- 1423 255	185.858
905	148 114	215.101	160.743	27.179	-1551.745	-1390.957	145.312
88	157.737	242.994	172.173	42.492	-1549.626	-1358.985	118,310
88	55.5	267.839	84.099	58.632		-1327.426	99.054
8	175.310	310 648	207.617	02.420	-1545.488	-1296.307	95.5
0001	179 075	329.321	218.867	110.455		-1235,369	64.529
200	182 004	346.523	229.700	128.505	-1689.825	-1196.287	56.807
20000	200	20000	011.04.7	19970		769 1511-	20.132
1249 000	179.912	410.154	245.059	206.204	CRYSTAL	AL <> LIQUID TRANSITION	<u> </u>
1300	179.912	417.354	251.677	215.379		-1109.665	44 587
94	179.912	430.687	263.994	233,370	-1621.773	-1070.051	39.924
3 5	716.61	45.039	22.617	797 707	-1616.227	-1030.837	35.897
36	170.912	454.711	286.503	269,353	-1610.764	-991.989	32,385
1800	179.912	475 901	306.271	305.335		-911.869	26.463
006	179 912	485.629	315.457	323,326		-871.010	23.946
2000	179 912	494.857	324.198	341.318	-1639.109	-830.438	21.689
3300	179 912	503.635	332.535	359.309	_	-790 137	19.654
2022	170 917	\$20,004	340,304	305,701		-750.091	17.809
2400	179.912	527.659	355.458	413.282	-1617.876	-670.713	16.131
2500	179.912	535.003	362.494	431.274	-1612.720	-631.354	13.191
2800	179.912	542.059	369.265	449.265	-1607.634	-592,200	11.897
2800	70.912	555 302	375.791	467.256	-1602.623	-553.240	10.703
2002	179.912	561.706	388 175	503.247	7607661-	- 514,464	9597
3000	179.912	567.805	394.062	521230	-1588.095	-437.429	7.616

K204S1(cr)

CURRENT: June 1978

Standard State Pressure = p^* = 0.1 MPa

kl-mol-

 $H^{\circ}-H^{\circ}(T_{i})$

S -[G*-H*(T,)]/T

ů

Σ¥

-K-lmol-1

INFINITE

0 175.544 216.494 281 186 334,580 348.575 38.856

0. 79.195 110.667

0 200 298.15

131,319

229.634 166.909 129.153 103.978 86.012

-1278.152 -1319,595 -1318,862

-1437.723 -1445.229 -1446.060

175.546 180.911 191.544 175.544

176.357

131.666 147.649 160.733

-1437.706

Ö

-1194.353 -1152.659 -1111.361

-1443.295 -1488.244 -1481.100

204.005 217.031 230.132 237.547 243.098

172.527 186.368 199.619

212.865

207.169

300 400 500 600 700 800 800 1000 11100

-1445.397

0.243 14.233 29.663 46.309 64.259 83.558

--- ALPHA <---> BETA

95.151

354.737 231.188

-1427.199 -1433.305 -1436.295

NFINITE

62.072 53.454 46.001 39.570

-1069.491 -1023.335 -968.729

-1630.753

CRYSTAL(a)

M_r = 174.2542 Potassium Sulfate, Alpha (K₂SO₄)

Enthalpy Reference Temperature = T, = 298.15 K $\Delta_t H^{\circ}(0 \text{ K}) = -1427.20 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta_1 H^{\circ}(298.15 \text{ K}) = -1437.71 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1}$

Potassium Sulfate (α-K₂SO₄)

 $\Delta_{\rm rr} H^{\circ}(\alpha \to \beta) = 8.452 \pm 0.418 \text{ kJ} \cdot \text{mol}^{-1}$

correcting the observed voltage for the formation of the K-amalgam, and converting to absolute volts, we have Ex = 3.59172 volts for the Taking $\Delta_i G^0(H_{25}SO_4, \text{ cr. } 298 \text{ 15 K}) = -149.658 \text{ kcal-mol}^{-1}$ and reference entropies from, we calculate $\Delta_i G^0(K_2SO_4, \text{ cr. } 298.15 \text{ K}) = -343.525 \pm 0.2 \text{ kcal mol}^{-1}$. Shibata et al., measured the emf of the cell K (amalgam, 0.2201%)IK,SO4(sat. soln.), Hg,SO4IHg at 298 303 K. From their results at 298 K, reaction at 298 K, 2 K(cr) + Hg.SQ(cr) = 2 Hg(l) + K.SQ(cr). From this voltage, we calculate A,G'(298.15 K) = -165 656 kcal mol⁻¹. $S^{\circ}(298.15 \text{ K}) = 175.544 \pm 0.8 \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ Enthalpy of Formation $_{\rm cr}(\alpha \rightarrow \beta) = 857 \pm 1 \, {\rm K}$

Source (2) Solution at infinite dilution, $\Delta_c H^2(K_2SO_a, cr. 298.15 \, K) = 5.677 \pm 0.020 \, kcal-mol⁻¹, adopted in this tabulation is based on our reanalysis of the enthalpy of solution measurements of Mishchenko and Pronina, Tsvetkov and Rabinovich, Romanova and Samoilov, Cohen and Kooy, Bronsted, Samilov et al., ⁹ and Gritsus et al. ¹⁰ Enthalpies of dilution are taken from Lange and Streeck. ¹¹ When$ this result is combined with enthalpy of formation of the infinitely dilute ions from CODATA, we obtain $\Delta_t H^2(K_sSO_s, aq, \infty)$ 298.15 K) = -337.940 ± 0.10 kcal-mol⁻¹ and $\Delta_t H^o(K_sSO_4$, cr. 298.15 K) = -343.617 ± 0.10 kcal-mol⁻¹. The solubility of K_sSO_4 (cr) in water at 298 K has been measured by many workers. $^{412.14-16}$ When the solubility of 0.6919 molal is combined

with the activity coefficient data of Stokes, ¹⁹ we obtain $\Delta_1G^{\circ}(298.15 \, \text{K}) = 2423 \pm 20$ cal-mol⁻¹ for the reaction $K_2SO_4(cr) = 2 \, \text{K}'(4q, \alpha) + SO_4$, ²(aq, α). When this result is combined with enthalpies of formation and entropies from, ³ we obtain $\Delta_1H^{\circ}(K_2SO_4, cr, \alpha) + SO_4$, ²(aq, α). When this result is combined with enthalpies of formation and entropies from, ³ we obtain $\Delta_1H^{\circ}(K_2SO_4, cr, \alpha) + SO_4$. 298.15 K) = 343.595 ± 0.2 kcal·mol⁻¹

We adopt the value of $\Delta_t H^0$ (298.15 K) obtained from the enthalpy of solution measurements.

Heat Capacity and Entropy

Low temperature heat capacities of $K_2SO_4(ct, \alpha)$ have been measured by Moore and Kelley¹⁷ from 52.7-295.4 K and by Paukov¹⁸ from 12.5-299.5 K. The heat capacities reported by Moore and Kelley are systematically lower by about 0.5% than those of Paukov. Our adopted value of $S^0(298.15 \text{ K}) = 41.956 \pm 0.2$ cal·K⁻¹ mol⁻¹ is based on $S^0(12.5 \text{ K}) = 0.068 \text{ cal·K}^{-1} \text{ mol}^{-1}$ is and $H^0(12.5 \text{ K}) - H^0(0 \text{ K}) = 0.640$ cal-K-1-mol-1 derived from a Debye T3 law extrapolation.

Heat capacity data measured by adiabatic calorimetry in the range 298.5-773.7 K have been reportd by Shmidt.19 In addition, drop calorimetric measurements have been reported by the following workers; Shomate and Naylor, 20 Dworkin and Bredig, 21 Denielou et al., 22 and Rubinchik et al. 22 The heat capacity and enthalpy curves between 298 K and 857 K are obtained by orthogonal polynomial curve fitting of all the data listed above. These data are in good agreement.

Transition Data

K₂SO₄(cr, α) is the low temperature form (sometimes denoted as K₂SO₄, II). The mineral is known as arcanite and exists in the form of orthorhombic crystals (space group D^{126} –Pnma).²⁴ The orthorhombic-to-hexagonal transition temperature for K₂SO₄ is selected as 857 ± 1 K from the calorimetric work of Dworkin and Bredig²¹ and Rubinchik *et al.*²² and the polymorphism study of Pistorius and Rapoport.25 The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of α and β-K₂SO₄ extrapolated to 857 K.

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Potassium Sulfate, Alpha (K₂SO₄)

Continued on page 1489

K2O4S1(cr)

Standard State Pressure = p = 0.1 MPa

Enthalpy Reference Temperature = T, = 29&15 K

J-K-1mol-1

2542 Potassium Sulfate, Beta (K2SO4)

log Kr

VC

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 $H^{\bullet}-H^{\bullet}(T_i)$ Δ_iH^{\bullet}

 $S^{*} - [G^{*} - H^{*}(T_{*})]T$

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ΤÆ

0 100 200 298.15

229.703 228 164 166.035 128.634 103.688 85.874 72.525

-1310 419 -1271.452 -1231.311 -1191 022 -1150 797 -1110 755

-1424.246 -1431.462 -1432.632

-1432.709 -1431.838

-1430.146

45.534 62.253 79.784 90.140

220.891 233.605 246.205 253.257

322,537 345 935

146.858 154.975 163 134 171 251 179 368 184,000

300 400 500 600 700 800 877 000

358.437 296.781

62.095 53.512 46.074 39.641 34.224

-1069.890 -1024.456 -970.268 -910.674 -851.747

- 1629 446 - 1621.806 - 1613 438

137.249 158 031 179.625 188.936

-- ALPHA <--> BETA

-1480.836 -1476.487

98.127

258.500 270.423 281.957 293 114 303.914 308.349

367.530 387.703

406 729 424 807 442 087 449.136

900 187.485 1000 195.602 1100 203.761 1200 211.878 1300 223.38 1400 228 112 1500 236.229

--- BETA <--> LIQUID

-1604.337 -1594.495

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CRYSTAL(B)

Potassium Sulfate (B-K₂SO₄)

 $\Delta_t H^{\circ}(298 \text{ 15 K}) = [-1424.243] \text{ kJ mol}^{-1}$ $\Delta_{\rm tr} H^{\circ}(\alpha \to \beta) = 8.452 \pm 0.418 \text{ kJ mol}^{-1}$ $\Delta_{\rm trr} H^{\circ}(\beta \to 1) = 34.392 \text{ kJ mol}^{-1}$ 5°(298 15 K) = [192.279] J K⁻¹·mol⁻¹ $f_{tot}H^{\circ}(\beta \to 1) = 1342 \pm 1 \text{ K}$ $_{in}(\alpha \rightarrow \beta) = 857 \pm 1 \,\mathrm{K}$

Enthalpy of Formation

 $\Delta H'(K_2SO_a, \alpha, \beta, 298.15 K)$ is calculated from $\Delta H'(K_2SO_a, \alpha, \alpha, 298.15 K)$ by adding the enthalpy of transition ($\alpha \rightarrow \beta$), $\Delta_m H'$, and the difference in enthalpy, H'(857 K)-H'(298.15 K), between the alpha and beta crystalline forms.¹

High temperature enthalpy measurements by drop calorimetry were carried out by Shomate and Naylor, 872.4-1258 8 K), Rubinchik et al., 3850-1340.7 K) Dworkin and Bredig, 4868.5-979.9 K), and Denielou et al., 5864-1300 K). The data of are systematically higher by about 0.5% than the data from. 3 C, values are derived from the smoothed curves and extrapolated to 298 15 K and 1500 K. S'(K,SO4, B, 298 15 K) is calculated in a manner analogous to that used for the enthalpy of formation. Heat Capacity and Entropy

Transition Data

The high temperature B-modification of K₂SO₄ is of hexagonal structure, space group D³_{3c}-P3ml.* The transition from the low temperature orthorhombic pseudohexagonal modification occurs at 857 ± 1 K.1

The adopted melting point of 1342 K was determined by Shomate and Naylor² and Rubinchik et al.³ The heat of fusion, $\Delta_{hd} J^{o} = 8 220 \pm 0.400$ kcal mol⁻¹, is calculated from the difference between the smoothed relative entialpy of the liquid (refer to the $K_2SO_4(1)$ table) and the adopted enthalpy value for the β -crystalline form at T_{tus} .

M. Rubinchik, E. I Banashek, V. A. Sokolov, and A. I. Fomin, Russ J Phys Chem. 45, 599 (1971).
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JANAF Thermochemical Tables: K₂SO₄(cr, α), K₂SO₄(l) 6-30-78. ²C. H. Shomate and B. F. Naylor, J. Amer Chem. Soc. 67, 72 (1945).

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Potassium Sulfate (K₂SO₄)

LIQUID

 $S^{\circ}(298.15 \text{ K}) = [211.505] \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ $T_{\text{los}}(\beta \to l) = 1342 \pm 1 \text{ K}$ Torn = 2567 K

Enthalpy of Formation

Δ_H"(K₅SO₄, 1, 298.15 K) is calculated from Δ_H"(K₅SO₄, β, 298.15 K) by adding the enthal enthalpy, H"(1342 K)-H"(298.15 K), between the β-crystal and liquid.

Heat Capacity and Entropy

transition at 800 K. Below the glass transition, the heat capacity is taken as that of the orthorho and Rubinchik et al. (single point at 1344.84 K). A constant heat capacity of 46.15 cal·K⁻¹·n Enthalpies for K2SO4(1) have been measured by drop calorimetry by Shomate and Naylor (1358 S°(K₂SO₄, I, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of

Fusion Data

Refer to the K2SO4(cr, \(\beta \)) table for details.

Vaporization and Decomposition Data

Tables, ! Molecular vaporization data are discussed on the $K_2SO_4(g)$ table. $T_{v\mu\nu} = 2975$ K is the energy difference is zero for the reaction $K_2SO_4(I) = 2 K(g) + SO_2(g) + O_2(g)$. Decomposition to cantly lower decomposition pressures than decomposition to the metal. Significant decompositio pressures from the two processes are of comparable magnitude in the vicinity of the melting point of K₂SO₄(cr)⁵⁶ are in good agreement with dissociation pressures and the heat of reaction ca K₂SO₄(I) can vaporize to the gaseous monomer K₂SO₄(g) or decompose according to K₂SO according to $K_2SO_4(1) + H_2O(g) = 2 KOH(g) + SO_2(g) + 1/2 O_2(g)$.

JANAF Thermochemical Tables: K₂SO₄(cr, α), K₂SO₄(cr, β), K₂SO₄(g), 6-30-78. ²C. H. Shomate and B. F. Naylor, J. Amer. Chem. Soc. 67, 72 (1945).

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K₂O₄S₁(cr,I)

CURRENT June 1978

(*)
te (K ₂ S
n Sulfa
Potassiun

(K ₂ SO ₄)
Sulfate (
Potassium
174.2542
M.

| C; S; -[G*-H(T,)] T H*-H(T,) AHT 0

 | C; S - [O*-HY(T)]JT H"-HP(T, Latt) AH* 0 0 INTENTITE -25 456 -1471.199 110.667 127.344 186.200 -11.915 -146.225 111.319 175.344 115.544 0 -1431.305 117.679 216.694 180.911 142.323 -1445.225 117.571 218.186 20.433 -1445.229 -1446.000 117.577 218.186 20.433 -1445.229 -1446.000 117.577 218.186 20.403 -1445.239 -1445.239 118.583 20.403 4.62.39 -1445.239 -1445.239 118.603 30.827 217.031 64.239 -1445.239 118.603 30.837 230.137 85.239 -1445.239 118.703 34.837 237.547 101.603 -1445.239 118.703 34.537 245.341 -160.246 -143.235 118.703 34.2487 25.158 -143.235 111.87 44.50.43

 | C\$ S -(f° - HT/T))IT H'-HI-TI ALT AG* 0 0 NNFWITE -25 46 -147.199 -147.199 -147.199 19.195 61 609 ZT7387 -119.18 -143.205 -139.431 19.195 117.344 186.200 -119.18 -143.205 -139.543 19.196 17.344 186.320 -141.772 -119.532 -138.245 19.10 20.0870 19.544 20.043 -147.773 -119.832 16.53 176.544 180.911 142.33 -1445.205 -127.812 17.53 20.5870 19.544 29.663 -1445.205 -127.812 17.54 20.507 144.205 -127.812 -118.205 -118.202 17.54 20.507 44.205 -144.205 -119.433 111.30 20.71 34.348 2.0.132 85.24 -149.205 -119.433 20.71 34.348 2.0.132 85.131 -149.205 -119.433

 | C\$ S -(f° - HT/T))IT H"-HI-TI, b.H" AG* 10.067 173.34 186.290 -11578 -1437.199 -1477.199 19.195 61 609 277.34 -15.48 -1477.199 -1477.19 13.19 175.34 175.34 0.24 -1477.20 -1138.23 13.19 175.34 175.34 0.24 -1477.20 -1138.23 140 25.35 145.20 -1437.70 -1138.82 16.69 175.44 10.54 0.24 -1477.20 -1138.82 16.60 175.44 10.54 0.24 -1477.20 -1138.82 16.50 25.50 19.54 29.63 -146.20 -174.12 17.57 281.18 204.03 46.209 -144.23 -119.433 17.57 281.18 204.03 46.209 -144.23 -119.433 29.50 23.13 42.20 -144.23 -119.433 20.14 23.25 23.13 -144.23 -119.433 | C, S = -(G*-HYT) JT H*-HPT, AHT ALG* 0. 0. T77387 -12578 -147199 -147199 110.667 127344 186.200 -11915 -145.229 -1471199 110.67 127344 186.200 -11915 -145.229 -1193.843 111.139 175.344 186.200 -14170 -1193.843 -1193.843 117.69 216.694 189.911 14233 -1445.229 -1278.132 117.534 117.534 0.243 -1475.229 -1278.132 -1193.843 117.549 216.694 189.911 14233 -1445.229 -1278.132 117.549 216.694 189.911 -1445.229 -1278.737 -1145.229 -1745.229 117.541 219.003 46.209 -1445.209 -1176.139 -1445.209 -1176.139 118.548 219.003 46.209 -1445.209 -1176.239 -1116.839 -1116.839 -1116.839 -1116.839 -1116.839 -1116.839 -1116.839 -1116.839

 | C\$ S -(f° - HT/T))IT H"-HI-TI ALT AG 10.067 177.34 186.290 -11378 -113730 -1136.41 19.641 19.195 61 609 277.34 -12.578 -1437.305 -138.245 13.19 175.34 175.34 0.24 -1477.20 -138.245 13.19 175.44 175.34 0.24 -1477.20 -138.235 16.69 175.34 0.24 -1477.20 -138.235 16.60 175.44 175.44 0. -1437.70 -138.235 16.60 175.44 2.6.30 -1447.20 -138.247 17.57 281.186 204.03 -1445.20 -1194.333 17.57 281.186 204.03 -1445.37 -1194.333 17.57 281.186 204.23 -1443.23 -1194.333 186.26 345.80 23.13 84.23 -1443.23 -1194.333 187.26 345.80 23.13 13.24 -144.32 -1194.333
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| 203 761 405 779 269 718 150 713 -1629 446 2111878 442 807 293 357 191 3039 -1613 489 2123.38 442 087 293 316 200 400 -1613 438 201.460 443 718 298 316 200 400 -1613 438 201.460 487 187 318 105 286 523 -156 452 201.460 510 189 320 486 -156 452 -156 452 201.460 510 189 320 788 -156 452 -156 452 201.460 510 189 320 788 -156 452 -156 452 201.460 510 189 320 788 -156 452 -156 452 201.460 510 189 320 788 -156 452 -156 452 201.460 543 319 17 349 207 -154 457 -151 127 201.460 543 319 17 349 320 -151 127 -151 127 201.460 543 319 17 349 320 -151 127 -151 127 201.460 543 319 17 349 320 -151 127 -150 126 <td>203 761 405 779 269 718 150 713 -1629 446 2111.878 424.877 281.835 171.436 -1611.805 219.336 424.877 281.835 171.436 -1611.438 219.336 449.136 288.316 202.400 </td> <td>203.761 46.577 269.718 159.713 -1629.446 -970.268 219.995 442.867 281.895 119.44 -161.846 -910.674 213.38 442.087 281.895 119.49 -161.348 -831.747 223.38 449.15 288.316 272.400 BETA <> LIQUID 201.460 483.287 288.316 276.200 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 | 203.761 466.779 269.718 150.713 -1629.446 -970.268 2115.784 442.887 281.885 177.44 -161.180 -910.674 212.384 449.136 298.316 202.400 -161.180 -811.747 201.460 474.763 298.316 202.400 -161.818 -811.747 201.460 497.187 310.880 286.623 -156.438 -794.930 201.460 497.187 318.105 286.623 -156.438 -794.390 201.460 510.189 329.708 288.759 -151.345 -794.390 201.460 513.917 340.688 308.915 -155.438 -575.037 201.460 53.3197 340.688 309.01 -154.468 -575.639 201.460 53.51.43 369.33 -151.174 -469.774 201.460 53.51.44 369.33 -151.174 -469.774 201.460 53.51.44 369.33 -151.174 -469.774 201.460 53.51.44 | 203.761 466.779 269.718 150.713 -1629.446 -970.268 2115.784 442.887 281.885 117.44 -161.180 -910.674 212.384 449.136 298.316 202.400 -161.180 -811.741 201.460 474.762 298.316 202.400 -161.87 -101.101 201.460 477.187 305.894 28.677 -157.135 -794.59 201.460 510.189 329.708 286.623 -156.452 -739.730 201.460 510.189 329.708 286.63 -155.136 -739.730 201.460 513.917 340.688 308.915 -154.678 -576.639 201.460 534.899 361.017 349.277 -154.678 -576.639 201.460 544.809 361.017 349.349 -155.136 -376.639 201.460 544.809 361.017 349.349 -152.337 -416.833 201.460 544.809 361.017 349.349 -152.337 -416.833 <

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 | 201.460 574.344 388.142 409.644 -1512.387 201.460 574.344 388.142 409.644 -1519.101 201.460 574.344 388.434 409.576 -1512.892 201.460 500.997 412.064 470.082 -1506.719 201.460 600.997 412.064 470.082 -1506.719 201.460 615.607 425.74 510.274 -1488.888 201.460 622.929 433.457 530.520 -1483.129

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 | 201.460 383.733 444.400 449.350 -1512.832 -1512.833 201.460 501.873 444.400 449.350 -1505.753 -239.747 201.460 600.997 412.064 470.082 -1507.79 -207.913 201.460 607.999 419.449 490.228 -1494.762 -1563.18 201.460 605.299 449.113 530.250 -1483.159 -133.79 201.460 622.998 449.113 550.666 -1477.463 -2.853 | 201.460 38.1.279 4.8434 42.970 -1511.833 2.813.83 2.01.460 600.971 412.064 479.35 -1505.753 -239.747 201.460 600.977 412.064 479.082 -1507.79 -207.913 201.460 607.999 419.449 490.228 -1494.762 -155.318 201.460 615.202 42.574 510.774 -1488.889 -164.951 201.460 622.999 440.113 550.666 -1477.463 -2.853 201.460 622.999 440.113 550.666 -1477.463 -2.853

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 | - 100 LP - 1 | - 15/7 (15/17) - /15/17/5 (15/15/15/15/15/15/15/15/15/15/15/15/15/1 |
| 201.400 030.626 440.337 370.812 -1471.903

 | 10 1/2/2 /1X 1/2 /1X 1

 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
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 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
 | - 100/7 - 100/17 - 10
 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903
 | - 100/7 - 100/17 - 10 | - 100/7 - 100/17 - 10 | - 110/7 VI 11/7 / 11/1/2 VI 11/7 VI 11 | - 100/75 - 100/100 - 100/100 POST - |
| COST/61 - 7100/6 /CCO++ 0700CO CO+-107

 |

 | 10674 COC1141 - 710016 155000 00000 000100

 | 10674 COC1141 - 710016 155000 00000 000100 | 10674 COC1141 - 710016 155000 00000 000100

 | 10674 COC1141 - 710016 155000 00000 000100
 | - 10574 - 5057741 - 719076 /5moth 679000 000-107

 | 10674 COC1141 - 710016 155000 00000 000100
 | 18/4 (18/14) - 7100/5 /500m 87000 00-107
 | - 10574 - 5057741 - 719076 /5moth 679000 000-107
 | , 15/7 (5/7) 15/7/
(5/7) 15/7/ | 18/4 (18/14) - 7100/5 /500m 87000 00-107 | - 10574 - 5057741 - 719076 /5moth 679000 000-107
 | - 10574 - 5057741 - 719076 /5moth 679000 000-107
 | , 15/7 (5/7) 15/7/ | , 15/7 (5/7) 15/7/
 | | - 10574 - 5057741 - 719076 /5moth 679000 000-107 |
| COCT 141 - 710016 10000 00000 00000

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 | 106'14 COS'141 718'01'S 10'70'S 07'70'S 07'70'S

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 | IDE'T COCITED TIGORE STORE CONTROL
 | 10674 COCTABL 710076 FORDER CTOCK CO. CO.

 | 106'14 COS'141 718'01'S 10'70'S 07'70'S 07'70'S
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| COST/61 - 7100/6 /CCO++ 0700CO CO+-107

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 | 10674 COC1141 - 710016 155000 00000 000100

 | - 10674 COC1141- 719016 1500th 679000 00-107 | - 10674 COC1141- 719016 1500th 679000 00-107

 | - 10674 COC1141- 719016 1500th 679000 00-107
 | - 10574 - 5057741 - 719076 /5moth 679000 000-107

 | 10674 COC1141 - 710016 155000 00000 000100
 | 18/4 (18/14) - 7100/5 /500m 87000 00-107
 | - 10574 - 5057741 - 719076 /5moth 679000 000-107
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 | - 10574 - 5057741 - 719076 /5moth 679000 cot-107
 | , 15/7 (5/7) 15/7/ | , 15/7 (5/7) 15/7/
 | | - 10574 - 5057741 - 719076 /5moth 679000 cot-107 |
| 201.400 050.026 440.357 570.812 - [4/1.903

 | 10 1/2/2 /1X 1/2 /1X 1

 | 201.40 050.626 440.357 570.812 -[4/1.303 4/.30]
 | 201.40 050.626 440.357 570.812 -[4/1.303 4/.30]
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 | 201.40 050.626 440.357 570.812 -[4/1.303 4/.30]

 | - 100.45 050.050 050.051 050.051 050.051
 | 201.40 050.626 440.357 570.812 -[4/1.303 4/.30]
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 | - 100.45 050.050 050.051 050.051 050.051 | 201.40 050.026 440.357 570.812 - [4/1.303 4/.30]
 | 201.40 050.026 440.357 570.812 - [4/1.303 4/.30]
 | - 100/7 - 100/17 - 10 | - 100/7 - 100/17 - 10 | - 110/7 VI 11/7 / 11/1/2 VI 11/7 VI 11 | - 10574 - 1067141 - 710701 157044 070700 00+107
 |
| 201.400 030.626 440.337 370.812 -1471.903

 | 10 1/2/2 /1X 1/2 /1X 1

 | - 100.45 050.050 050.051 050.051 050.051
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 | - 100/7 - 100/17 - 10 | - 100/7 - 100/17 - 10 | - 110/7 VI 11/7 / 11/1/2 VI 11/7 VI 11 | - 100/75 - 100/100 - 100/100 POST - |
| 201.400 636.628 446.337 5/0.812 -14/1.903

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

 | 201.400 636.828 446.337 570.812 -1471.903 47.901

 | 201.400 636.828 446.337 570.812 -1471.903 47.901 | - 100.45 050.050 050.051 050.051 050.051

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 | 201.400 636.828 446.337 570.812 -1471.903 47.901
 | 201.400 636.828 446.337 SIUXII - 14.11 WIR
 | 201.400 636.828 446.337 570.812 -1471.903 47.901 | 201.400 636.828 446.337 570.812 -1471.903 47.901
 | 201.400 636.828 446.337 570.812 -1471.903 47.901
 | 201.400 636.828 446.337 SIUXII - 14.11 WIR | 201.400 636.828 446.337 SIUXII - 14.11 WIR
 | - 100 LP - 1 | - 100/75 - 100/100 - 100/100 POST - |
| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

 | 201.400 636.828 446.337 SIUXII - 14.11 WIR

 | 201.400 636.828 446.337 SIUXII - 14.11 WIR | - 100/7 - 100/17 - 10

 | 201.400 636.828 446.337 SIUXII - 14.11 WIR
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| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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 | 201.400 636.828 446.337 SIUXII - 14.11 WIR | - 100/7 - 100/17 - 10

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 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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 | 201.400 636.828 446.337 SIUXII - 14.11 WIR | - 100/7 - 100/17 - 10

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| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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| 201.400 030.626 440.337 370.812 -1471.903

 | 10 1/2/2 /1X 1/2 /1X 1

 | - 100.45 050.050 050.051 050.051 050.051
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 | - 100.45 050.050 050.051 050.051 050.051
 | - 100/7 - 100/17 - 10 | - 100/7 - 100/17 - 10 | - 110/7 VI 11/1 - / IXII/C / C 077 V/OXD (07/10/7
 | - 100/75 - 100/100 - 100/100 POST - |
| 201.400 636.628 446.337 5/0.812 -14/1.903

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

 | 201.400 636.828 446.337 570.812 -1471.903 47.901

 | 201.400 636.828 446.337 570.812 -1471.903 47.901 | - 100.45 050.05 440.35/ 5/0.812 - 14/1.903

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| 201.480 030.828 446.337 - 14.11.4013

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| 201.480 030.828 446.337 - 14.11.4013

 | 711 401 DEC X/X AAD X/Y - 1/X/11 UNIX

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CRYSTAL(α−β)-LIQUID

Potassium Sulfate (K₂SO₄)

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

Refer to the single phase tables for the alpha, beta, liquid phases for details.

K crystal, alpha K crystal, beta K liquid

0 to 857 P 857 to 1342 P above 1342 to T_{dem} P

Potassium Sulfate (K₂SO₄)

Potassium Sulfate (K₂SO₄)

 $S^{\circ}(298.15 \text{ K}) = 366.152 \pm 16.7 \text{ J·K}^{-1} \cdot \text{mol}^{-1}$

IDEAL GAS

M_r = 174.2542 Potassium Sulfate (K₂SO₄)

(50,S1(g)

and Degeneracies	E 1098 (2) 613 (2) [230](2) [62](2)
ibrational Frequencies, Symmetries, and Degeneracies, cm ⁻¹ v, cm ⁻¹	B ₁ [450] (1) B ₂ 1124 (1) 639 (1) [262](1)
Vibrational Freq	A ₁ 962 (1) [458](1) [190](1)

Bond Distances: S-O = 1.47 Å K-O = 1.45 Å Bond Angles: O-S-O = 109.47 O-K-O = 58.67 Ground State Quantum Weight: [1] Point Group: D.

9=4

Product of the Moments of Inertia: $I_A/BJ_C = 2.626307 \times 10^{-112} \text{ g}^3 \cdot \text{cm}^6$

Enthalpy of Formation

The adopted value of the enthalpy of formation is based on JANAF analyses of the vaporization data given below. Earlier data on vaportzaiton of K₂SO₄ is extremely discordant (for a review, refer to reference ¹⁰). Dissociation and other reactions play an important in K₂SO₄ vaportzaiton (refer to the K₂SO₄(t) table).

Torsion-effusion studies on the vaporization of K₂SO₄(g) by Lau et al.³ showed an orifice dependence which was reproduced in separate runs. Plante et al. ² did not observe this orifice size dependence in their effusion study, obtaning similar total pressures in two sep experiments. Calculated dissociation pressures were subtracted in both studies to obtain K₂SO₄(g) pressures. Similar results were obtaine Efimova and Gorokhov. We have corrected the effusion data of Kosugi¹¹ for dissociation. The 3rd law enthalpy of sublimation from the 1 studies¹⁻³ are in very good agreement indicating similar K_{20} O(g) pressures. The studies of Lau et al.³ and Efimova and Gorokhov¹ yield

Lau et al.3 and Efimova and Gorokhov also carried out mass spectrometric measurements of the K₂SO3 ion intensity as a functic temperature. The 2nd law enthalpy of sublimation of Lau et al. 3 obtained in two separate mass spectrometric experiments tend to corrob their 2nd law enthalpy from the torsion-effusion measurements. The 2nd law enthalpy of Efirnova and Gorokhov' as well as that of Fic. et al. 12 are more in line with our 3rd law effusion values. Kosugi¹¹ did not observe the K₂SO², ion in his mass spectrometric experiments. law enthalply of sublimation (from K₂SO₄(cr, β)) some 6 kcal-mol⁻¹ greater than our calculated 3rd law enthalpy. appearance potential of $K_2SO_2^*$ has been measured as 7.40 \pm 0.5 eV, 12 8.40 \pm 0.3 eV³ and 8.0 eV. 1

We have discounted the transpiration experiments of Halstead¹³ and Dubois and Millet. ¹⁴ The calculated 3rd law Δ_H^0 (298.15 K) may I an uncertainty of 3 kcal·mol⁻¹ since the JANAF Gibbs energy functions are partially based on the estimated molecular constants of K₂SO Our adopted Δ_H^0 is based on a weighted average of the 3rd law results from. ¹⁻³

					5			100 CO 1000 CO 10011 4
Source	Method	Reaction*	7/K	Data Points	6S cal·K ⁻¹ ·mol ⁻¹	2nd law	K), kcal·mol · 3rd law	Δμ'(298.15 K), kcal·mol · Δμ'(K ₂ >O ₀ , g., 298.15 K) 2nd law 3rd law kcal mol ⁻¹
Efimova ¹	effusion	V	1171-1331	1	4.38	84.77	79.02 ± 0.11	-261.38 ± 1.5
Lau et al.3	torsion-	۷	1180-1274	37	5.18	85.36	78.93 ± 0.45	-261.47 ± 1.5
	effusion							
Plante ²	effusion	٧	1166-1322	56	-1.42 ± 0.8	77.03 ± 0.9	78.78 ± 0.42	
Plante ²	effusion	∢	1196-1321	15	-0.76 ± 2.0	77.87 ± 2.0	78.83 ± 0.51	
Halstead	effusion	<	1180-1340	٠	1.07	75.75	74.39 ± 0.15	
Kosugi	effusion	В	1409-1530	.12	2.70 ± 2.8	73.67 ± 4.2	69.66 ± 0.76	
Efimova!	mass spec	۷ ،	1171-1331	ć	1	78.0 ± 1.0	ı	-262.4 ± 2
Lau et al.3	mass spec	V	1183-1248	6	1	84.12 ± 2.02	1	-256.28 ± 2.0
Lau et al.3	mass spec	V	1180-1314	01	1	81.96 ± 0.40	1	-258.44 ± 1.5
Ficalora 12		4	1080-1230	٠	ı	79.8 ± 2.0	ı	-260.6 ± 4
	Reactions: 4) K ₂ SO ₂ (cr, β) = K ₂ SO ₂ (g	(S)	B) K ₂ SO ₄ ($(X_2SO_4(1) = K_2SO_4(g))$		

Heat Capacity and Entropy

Na.SO., The molecule can be pictured as having a central sulfur atom surrounded at the comers of a tetrahedron by four oxygen atoms with PREVIOUS. June 1978 (1 atm) oridging potassium atoms between two pairs of oxygens forming two planar mutually perpendicular KO₂S rings. The sulfate core is fairly symmetry is supported by the similar work of Ugarov et al. on Cs.SO, and the IR and Raman study of Atkins and Gingerich⁷ on Ks.SO. The adopted structure (Das symmetry) is based on the high temperature electron diffraction study of Spiridonov and Lutoshkin.⁵

l-lou	Enthalpy R	eference Te	emperature	Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$ 1.8^{-1}	sæ!	Standard Sta	Standard State Pressure = $p^* = 0.1 \text{ MPa}$ 1.11-1	p* = 0.1 MPa	
ion ion	TÆ	 ဗ	S - [G	-[G*-H*(T,)]/T	H*-H*(T,)	1	δ _G •	log Kr	
	200 co 200 co 250 co	0. 64.770 90.384 100.439	0. 273.209 326.456 347.734	INFINITE 449.682 375.546 367.897	-22.463 -17.647 -9.818 -5.041	-1080.636 -1085.784 -1090.608 -1092.515	-1080 636 -1070 071 -1052 380 -1042 597	1NF1NITE 558.948 274.854 217.839	
	298.15	108.730		366.152	ď	-1094.116	-1032.835	180.948	
	300	109.023	366.826 384 193	366.154 367.509	0.201 5.839	-1094.175	-1032.454 -1021.853	179.766	
	\$ \$ \$	122.342 127.380 131.555	400.128	370.604 374.713 379.416	11.809	-1104.063 -1105.903 -1107.600	- 1010.439 -998.632 -986.618	131.950	
	88	137 903	453.063	389.688	38.025	-1110.091	-962.173	83.765	
	888	145.525	493.901	410.835	66.452	-1113.351	-912.333	29.269	
	<u>88</u>	149.612	526.856	421.041	96.005	-1167.08 -1167.636	-854,758	4.648	
	0 1 1 2 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1	150.956 152.006	541.181 554.363	440.239 449.208	111.036	-1325.533 -1323.524	-814.251 -767.860	38.666 33.424	
,	1400 1400	152.842	566.564 577.917	457.772 465.953	141.430 156.749	1321 <i>.507</i> 1319.491	-721.636 -675.568	28.9% 25.206	
E the	1200	154.067	588.527	473.775	172.129	-1317.486	-629.644	21.926	
201	925	154.52	598.486 607.865	481.201	203.031	-1313530	-538.185	16.536	
four	0061	155.226	616.729	495.319 501.932	218.538	-1311.610 -1309.720	-492.632 -447.185	12.296	
parate	2000	155.736	633.111	508.293	249.637	-1307.873	-401.836	10.495	
three	2200 2200	155.940	640.715	514.419 520.326	265.221 280.824	-1306.075 -1304.332	-356.579 -311.405	7.394	
d 2nd	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	156.272 156.409	654.916 661.570	526.028 531.538	296.444 312.078	-1302.649	-266,310 -221,288	6.048 4.816	
,	2500	156.529	667.957	536.868	327.725	-1299.487	-176.330	3.684	
on of	2500 2700 2800 2800	156,637	674.099 680.012	542.028 547.030 551.882	343,383	-1298.017 -1296.630 -1295.330	-131.433 -86.591 -41.708	2.641 1.675 0.780	
calora s. The	288	156.896	691.218	556.592	390.415	-1294.124	2948	0830	
	3100	157.029	701.686	565.619	421.808	-1292.015	92,329	-1.556	
o (g).	3300	157.139 157.187	711.507	574.166 578.275	453.225 468.942	-1291.126 -1290.336 -1289.682	181.583 181.583 226.178	-2.874 -3.475	
	3500	157.231	720.756	582.281	484,663	-1289.155	270.753	-4.041	
	3,80 3,70 9,0	157.272	725.186	586.189 590.005	500.388	-1288.769 -1288.530	315,316 359,870	-4.575 5.080	
5 K)	8 8 8 8 8 8 8 8 8	157,343	733.691 737.779 741.764	593.731 597.372 600.932	531.850 547.586 563.325	- 1288.445 - 1288.523 - 1288.761	404.421 448.972 493.523	-5.559 -6.013 -6.445	
	4100	157.432	745.651	604.415	579,066	-1289.181	538.085	-6.855	
	8	157.481	753.150	61.160	610.558	-1290.615	627.252	-7.620	
	\$200	157.523	760.310	617.631	642.058	-1292.192	716.432	-8316	
	4 4 9 9 9 9	157.543	763.773	620.770 623.849	657.812 673.567	-1293.501	761.081	-8.642 -8.955	
	4800 4900	157.578	770.479	626.869	689.324	-1296.449	850.445 895.192	-9255 -9543	
	2000	157.609	776,912	632,743	720.842	-1300.452	939.979	-9.820	
	5200 5200	157.623 157.636	780.033	635.601 638.408	736.604	-1302.781	984.812 1029.689	-10.087	
	2300 2400 2500 2500	157.649	786.097	641.166 643.878	768.131 783.897 700.663	-1308.111	1074.621	-10.591 -10.830 -11.061	
	36.	157.687	704.778	649 165	815.431		1209 752	-11 284	
	2,200	157.693	797.569	651 744	831.200 846.969	-1320.800 -1324.621	1254.823	-11.708	
S Thus	2800 8000	157 711 157.720	803.007 805.658	656.780 659.239	862.740 878.512	-1328.659 -1332.909	1345.328	-11.911 -12.107	
s with	PREVIOUS: June 1978 (1 atm)	June 1978 ((1 atm)	;			CURRENT Ju	CURRENT June 1978 (1 bar)	

Continued on page 1489

K₂S₁(cr)

CRYSTAL

Potassium Sulfide (K₂S)

 $\Delta_t H^{\circ}(298.15 \text{ K}) = -376.56 \pm 12.6 \text{ kJ} \cdot \text{mol}^{-1}$

 $\Delta_{tus}H^{\circ} = 16.150 \pm 0.17 \text{ kJ} \cdot \text{mol}^{-1}$ Δ_{tr}H° = 0 kJ mol⁻¹

Standard State Pressure = p = 0.1 MPa

Enthalpy Reference Temperature = T, = 298.15 K

M_r = 110.2566 Potassium Sulfide (K₂S)

kJ·mol

 $H^{\bullet}-H^{\circ}(T_{i})$ $\Delta_{i}H^{\bullet}$

S -[G*-H*(T,)]T

ť

7,7

δÇ

46.606 46.606 36.536 29.787 24.952 21.318 18.427 15.867

-342.158 -334.377 -326.490 -317.488 -303.773

-388.349 -389.306 -389.826 -442.745 -438.078

15.602 23.773 32.105 32.105 32.105 40.749 50.053 11.364 71.364 71.364 77.673 893.908

115.061 118.023 123.702 130.167 135.757 143.224 149.486 155.672 153.8850 15

74,726 77,320 79,914 82,508 85,144 87,338 103,534 156,063 194,982 194,982 194,982 142,340

226.816 226.816 234.558 246.943 249.413 258.336 268.885 278.705

142,340

115.522 137.375 154.907 169.706 182.621 194.161 205.100

362.745 -362.659 -356.897 -349.730

-376.573 -384.524 -386.806

13,33

-281.577 -254.180

-586.914 -578.724

_ C, HUMP MAXIMUM TRANSITION

-- CRYSTAL <--> LIQUID

-227.467 -201.382 -175.879

-570.550 -562.393 -554.251

175.150 181.473 187.632

9.140 7.514 6.125 4.927 4.927 2.974 2.171

-150.920 -126.467 -102.492 -78.965 -55.863

-546.127 -538.021 -529.933 -521.866 -513.823

193.614 199.416 205.039 210.486 215.764

287.892 296.521 304.657 312.353 319.654

135.610 135.610 136.610 150.844 165.078 179.312 193.546 207.780

" = 1050 ± 10 K (diffuse lambda transition) $S^{(298.15 \text{ K})} = 115.06 \pm 16.7 \text{ J·K}^{-1} \cdot \text{mol}^{-1}$

Enthalpy of Formation

Flas = 1221 ± 10 K

Experimental measurements leading to the enthalpy of formation of $K_2S(cr)$ are summarized below.

Source	Reaction	Δ _t H*(298.15 K), kcal·mol ⁻¹
Sabatier'	Δ _{stn} H° K ₂ S(cr) and K(cr); Δ _n H° KOH(aq) + H ₂ S(aq)	-103.4
Rengade and Costeanu*		-87.3
Letoffe et al.?	H ₂ SO ₄ (aq, 1100 H ₂ O) + K ₂ S(cr) = K SO (soln.) + H S(g)	-92.1

a. The authors' value of -91.1 ± 0.9 kcal·mol⁻¹ is changed by new $\Delta_t H^0(298.15 \, \text{K})$ values for $H_2 SO_4(\text{aq}, 1100 \, \text{H}_2 \text{O})$, $K_2 SO_4(\text{cr})$ and $H_2 S(g)^{4.5}$

Since Sabater himself has expressed reservations because of impure material, we eliminate his value and adopt the average of the other two values, $\Delta_t H^o(K_2S, cr, 298.15 K) = -90 \pm 3 \text{ kcal·mol}^{-1}$.

Heat Capacity and Entropy

The heat capacity is taken from the drop calorimetry of Dworkin and Bredig (384 to 1260 K).* Between 298 and 820 K, the observed enthalpy differences and the constraint of passing through zero at 298.15 K are fit by a linear least squares technique; $C_p^* = 15.99 + 6.22 \times 10^{-3} \text{ T cal K}^{-1} \cdot \text{mol}^{-1}$ (298 820 K). The heat capacity in the observed diffuse lambda transition region, 820–1100 K, was adjusted to properly reproduce the observed enthalpies. The sharp heat capacity maximum occurs at 1050 K* and 46.60 cal·K -¹-mol -¹. From

1100 K to the melting point, 1221 K,7 the heat capacity was found to be constant at uccircl34.02 cal·K⁻¹mol⁻¹.

Freeman* has estimated S*(K₂S, ct, 298.15 K) = 27 cal·K⁻¹·mol⁻¹; Voronin* also has estimated 27 cal·K⁻¹·mol⁻¹. Kelley's additive entropy constants give 28.0 We adopt S*(K₂S, ct, 298.15 K) = 27.5 ± 4 cal·K⁻¹·mol⁻¹.

Transition and Fusion Data

A crystal II to crystal I transition at 419.6 K with a enthalpy change of 0.085 kcal·mol⁻¹ has been listed ¹⁰ from Bndgman, ¹¹ However, West¹² found no change in the x-ray powder diffraction pattern over the 298-473 K range. Although not definitive because of the small heat change listed, the drop calorimetric enthalpy measurements of Dworkin and Bredig⁶ do not show this transition. Therefore, we do not indicate any solid state transition at 419.6 K.

The diffuse lambda transition has been discussed above.

A melting point of 1221 K was determined by thermal analysis (cooling curves) of the $K-K_2S$ system by Dworkin and Bredig.⁷ This is considerably higher than earlier values of 1108 K^{13} and 1185 K^{14} but it is confirmed by their drop calometric measurements.⁶ A melting point of 1221 \pm 10 K is adopted with $\Delta_{lm}H^0 = 3.86 \pm 0.04$ kcal-mol^{-1.6}

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Potassium Sulfide (K₂S)

CURRENT: March 1978

K2S1(cr)

PREVIOUS

Standard State Pressure = $p^* = 0.1 \text{ MPa}$ k-mol ⁻¹	η° Δ _r G° log K _r		-346.506 -340.476 59 650 -346.519 -340.439 59 276 -354.470 -337.288 44 045 -355,759 -317,719 34.745		SS <> LIQUID_ TRANSITION	-565 757 -279 720 13.283 -561 705 -253 895 11.052	CRYSTAL <> LIQUID -557.669 -228.408 9.178 -553.649 -203.231 7.583	-178.341	-129.343	-537,742 -105,201 3,053 -533,813 -81,278 2,234 -579,907 -57,567 1,503	-34 040	-522.174 -10.702 0.254 -518.353 12.461 -0.283	35.458 58.299	-499.882 125.957 -2.350 -496.350 148.246 -2.670	170.414	
	$H^{\bullet}-H^{\bullet}(T_{r})$ $\Delta_{r}H^{\circ}$		0. – 340 0.138 – 340 7.741 – 354		ı		82.994 80.970 -557 101.066 -555			141.450 -537 151.546 -537 161.647 -537		191.930 -518		242.410 -499		
Enthalpy Reference Temperature = T_s = 298.15 K $1 \cdot K^{-1} m_0^{-1}$	S[G*-H*(T,)]T		141 172 141.172 141 634 141.174 163 487 144.136 181 019 140 815				262 640 194.667 268 969 198 992 276 451 204.261			301.824 223.241 307.282 227.521 317.461 231.640		326.571 243.124		346 431 259.856 349.974 262.903		
Enthalpy Reference Te	TK C;	0 100 200 250	298.15 74.684 300 74.726 400 77.320 500 70.914		00		1221 000 100 960 1300 100.960 1400 100.960			1800 1800 1800 1900 1900 1900 1900 1900		2200 100.960		2800 100.960 2900 100.960		
$\Delta_{\rm e}H^{\circ}(298.15 \text{ K}) = [-346.506] \text{ kJ·mol}^{-1}$	Δ _{luy} π = 10.150 ± 0.17 KJ·mol	a, $\Delta_{ta}H^{\circ}$, and the difference in enthalpy,	Bredig, ² (1221–1260 K) and is constant at < with C _p = 24.13 above this temperature	ation.												

LIQUID

Potassium Sulfide (K₂S)

 $S^{\circ}(298.15 \text{ K}) = [141.172] \text{ J·K}^{-1} \cdot \text{mol}^{-1}$ $T_{\text{ts}} = 1221 \pm 10 \text{ K}$

Enthalpy of Formation $\Delta_H^2(K_2S, 1, 298.15 \, K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{lm}H^2$, and the difference $H^0(1221 \, K)$ – $H^0(298.15 \, K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was derived from drop calorimetric enthalpy measurements by Dworkin and Bredig, 2 (1221–1260 K) and is $4.24.13 \, \text{cal·K}^{-1} \cdot \text{mol}^{-1}$ over the range measured. A glass transition temperature is assumed at 820 K with $C_p^a = 24.13 \, \text{above this termographer}$ and C_p^a equal to that of the crystal below this temperature. S°(K₂S, I, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

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° = 0.1 MPa	log Kr		63.551	63.145 46.606	36.536	24.952	21.318	- 1	13.371		9.178 7.583	5.018	3.053	1.503	0.847 0.254 -0.283	-0.772 -1.218	-1.627	-2.570 -2.670	70677
e Pressure = p	A _i G		-362.745	-362.659 -356.897	-349.730	-334,377	-326.490 -317.488	C, HUMP MAXIMUM TRANSITION	-281 <i>577</i> -254.180		-228.408 -203.231 -178.341	-153.717	-105.201	-57.562	-34.040 -10.702 12.461	35.458 58.299	80.991	125.957	41001
Standard State Pressure			-376.560	-376.573	-386.806	- 389.306	- 389.826 - 442 745	C, HUN	-586.914 -578 724	12	- 557.669 - 553 649 - 549 646	-545.660	-537.742 -533.813	-529.907	-526.026 -522.174 -518.353	-514.569	-507.125	-496,350	189765-
×	H°H°(T,)		oʻ	0.138	15.602	32.105	50.053	71.364	79.675 93.908	96.898	121.024 131.120	151312	171.504	191.696	201.792 211.888 221.984	232.080	252.272	282.560	00777
= 298.15	-[G'-H'(T,)]T		115.060	115.061	23.702	136.757	149.486	158.850	162.127	170.053	175.874 182.794 189.273	195.363	206.544	216,613	221.296 225.71 230.057	234.168	241.922	249.123	\$40°C7
Temperature = T,	S - [G		115 060	115.522	154.907	182.621	205.100	226.816	234.558 246.943	249.413	268.969 276.451 283.417	289.932	301.824	312,461	317.387 322.084 326.571	330.868	338.949	346,431	(Areas
	೮		74.684	74 726 71 320	97 508	85 144	103.554	194.982	142.340	142.340	100.960	100.960	100.960	100.960	100.960 100.960 100.960	100.960	100.960	096.001	
Enthalpy Reference	7.K	200 0 200 2	298.15	88	8	38	888	1050 000	1200	1221 000	0.65 0.05 0.05 0.05 0.05 0.05 0.05 0.05	0091	0081	2000	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	2400 2500	7200 7200 7200	7800 7800 7800 7800 7800 7800 7800 7800	

Potassium Sulfide (K₂S)

CRYSTAL-LIQUID

 $M_r = 110.2566$

0 to 1050 K*crystal 1050 to 1221 K crystal above 1221 K liquid

Potassium Sulfide (K₂S)

*There is a diffuse transition at 1030 K. Refer to the individual tables for details.

Continuation of discussions of selected K species

Potassium

Continued from page 1469

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F. T. Pistorius and E. Rapoport, J. Phys Chem. Solids 30, 195.

Continued from page 1485

rigid while the metal atoms undergo large amplitude motions. The internuclear distances of 1.47 Å for S-O and 2.45 Å for K-O are from 3 as are the O-S-Q and O-K-O angles. The principal moments of inertia are $I_A = 15.3096 \times 10^{-39}$ and $I_R = I_C = 130.9758 \times 10^{-49} \text{ g·cm}^2$.

Atkins and Gingerich? have observed the infrared and Raman spectra of K2SO, and Na2SO, isolated in oxygen and fundamentals are taken from the Raman study of Davies and Sandford.9 The low-frequency fundamentals involving Rb₅SO₄ and Cs₅SO₄ isolated in At, Kt, and Xe matrices at 4.2 K. Uncertainties in the location of the gas phase frequencies may contribute 4 cal·K⁻¹ mol⁻¹ to S°(298.15 K). nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. Good agreement exists between these observations and the frequencies adopted by Gurvich et al ⁶ The two other sulfate-10n group the metal atoms are taken from the infrared study of Belyæva et al.* These authors observed the spectra of K₂SO₄,

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