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Leo Brewer

November 1955

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ABSTRACT

The heats of sublimation of the elements at 298°K. to the various elemental gaseous species are tabulated.

HEATS OF SUBLIMATION OF THE ELEMENTS

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November 1955

In Paper 3 of Vol. 19B of the National Nuclear Energy Series, "The Chemistry and Metallurgy of Miscellaneous Materials; Thermodynamics" by L. L. Quill, McGraw-Hill, 1950, were tabulated various thermodynamic functions of the elements. Since the time that these values were compiled in 1945 with a minor revision in 1948, a considerable body of vapor pressure data has accumulated. The resulting changes in the values tabulated in Paper 3 have been quite minor except for some of the heats of sublimation, $\Delta H_V(298)$, tabulated in the last column of Table 3.6 on pages 26-27. In order to bring Paper 3 up to date, the recent vapor pressure data have been evaluated and the revised values are presented in this report.

It might be pointed out that not all of the available data have been evaluated with the thoroughness that they deserve. Eventually, it is hoped that all of the data will be adequately evaluated and revisions of this report will be issued from time to time as improved values are obtained. Undoubtedly some of the readers of this report have evaluated the available data for one element for some special purpose or they may have unpublished data. It would be a great help if they could forward any such information to be incorporated in future revisions of this report.

The values presented here have been treated in the same manner as those given in Table 3.6 of Paper 3. Whenever information has been available on the composition of the vapor, the vapor pressure data have been treated to yield data for the partial pressures of each individual species and the heats of sublimation given here are the ΔH values for the change in state from the solid form to the gaseous molecule indicated. Thus the ΔH_V given for Na represents the ΔH for the sublimation of one gram atom of Na solid to a mole of monatomic Na gas. The ΔH value given for Na_2 represents the ΔH for the sublimation of two gram atoms of Na solid to a mole of diatomic Na_2 gas. All heats given are heats of sublimation except for mercury which is liquid at 298°K .

One important addition to the method of presentation in Table 3.6 of Paper 3 is the indication of the uncertainty of the values tabulated. This is important because the uncertainties indicate the possible range of thermodynamic quantities that might be derived from these ΔH values.

The standard states for the condensed phases are the same as in Table 3.6 of Paper 3 with one exception. In the present tabulation, red phosphorous, the stable modification of phosphorus, has been taken as the standard state rather than white phosphorus. Thus in the present tabulation, the stable solid modification is taken as the standard state for all elements.

In the process of deriving the values of $\Delta H_V(298)$, it was sometimes necessary to use the heat of sublimation of 0°K . and values for $\Delta H_V(0^\circ\text{K})$ have been calculated for all the elements. However, this value is not tabulated here since it does not seem to be of sufficient value compared to $\Delta H_V(298)$ values. Whenever one has $(F-H_0)/T$

functions for which one would want ΔH values at 0°K ., one also has sufficient data to either readily convert the $(F-H_0)/T$ values to $(F-H_{298})/T$ values or to convert ΔH_{298} values to ΔH_0 values. However, when low temperature heat capacity data are lacking as is true in many instances, then only $(F-H_{298})/T$ values are available and only ΔH_{298} values are of interest. Since the very useful tabulations of K. K. Kelley (U.S. Bureau of Mines Bulletins 476 and 477) are set up for the direct calculation of $(F-H_{298})/T$ values, ΔH_{298} values would seem to be the most appropriate. Thus from his bulletins, one obtains $(F-H_{298})/T = (H_T - H_{298})/T - (S_T - S_{298}) - S_{298}$. The three quantities needed are tabulated in his bulletins.

No references are given in the present report, but a later revision of this report will contain references to be added to those in Paper 3 of Vol. 19B of the N.N.E.S. Most $-(F-H_{298})/T$ values have been improved so little that it is not worth tabulating them at this time and the ΔH values given here may be used directly with the free energy functions tabulated in Paper 3. It might be pointed out here that the headings of Table 3.6 on Page 27 are displaced one column as is obvious by inspection. Sufficiently improved free energy functions are available for three molecules to warrant listing them here for temperatures 298° , 500° , 1000° , 1500° , and 2000°K . respectively. They are as follows:
 Ti: 43.07, 43.71, 43.83, 47.44, and 48.69 and Zr: 43.33, ----, 46.60, 48.55, and 50.05. For the first three temperatures for S_8 we have 102.8, 107.1, and 123.2. For S_8 , $H_{298} - H_0 = 7542$. Professor John Margrave, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, has calculated free energy functions at close temperature intervals for all atomic species for which complete spectroscopic data are available. Thus

quite complete and accurate free energy functions will be available and the main uncertainty in thermodynamic calculations will be due to the uncertainty in the ΔH values. All ΔH values refer to changes between standard states and are ΔH_{298}° values although the superscript is omitted as it is obvious that all the thermodynamic quantities under discussion are standard values. The temperature designated as 298°K is an abbreviation for 298.15°K .

The values given for Ti, Cu, Ag, Zn, Cd, Sn, are those compiled in "Selected Values for the Thermodynamic Properties of Metals and Alloys," Minerals Research Laboratory, Institute of Engineering Research, University of California, Berkeley, California, 1955. Complete references are given in this compilation. The ΔH_{298} value given for Fe in the above compilation has been replaced by $99,000 \pm 1000$ calories on the basis of new unpublished work by Law McCabe, Carnegie Institute of Technology.

Table 1
Heats of Sublimation of Elemental Species at 298°K

	ΔH_{298} in kcals./mole		ΔH_{298} in kcals./mole
Li	38.35 ± 0.1	Mn	66.73 ± 0.5
Li ₂	50.6 ± 2	Re	186.2 ± 3
Na	25.90 ± 0.1	Fe	99 ± 1
Na ₂	33.8 ± 0.7	Co	102.0 ± 0.2
K	21.49 ± 0.1	Ni	101.75 ± 0.2
K ₂	30.7 ± 1	Cu	81.04 ± 0.5
Rb	20.5 ± 0.2	Ag	68.2 ± 0.4
Rb ₂	29.2 ± 1	Au	85. ± 1
Cs	18.8 ± 0.2	Zn	31.22 ± 0.05
Cs ₂	26.5 ± 1	Zn ₂	56. ± 1
Be	77.6 ± 0.4	Cd	26.78 ± 0.05
Mg	35.6 ± 0.3	Cd ₂	50.8 ± 1
Mg ₂	63.4 ± 0.7	Hg	14.652 ± 0.01
Ca	42.3 ± 0.1	Hg ₂	27.4 ± 0.3
Ca ₂	79 ± 1	Ga	66.2 ± 1
Sr	39.2	In	57 ± 2
Ba	42.0	Tl	42.8 ± 1
B	141. ± 3	C	170.89 ± 0.5
B ₂	213. ± 15	C ₂	195. ± 5
Al	77.5 ± 1.5	C ₃	200. ± 10
La	100 ± 5	C ₅	145. ± 15
Ce	96. ± 5	Si	105. ± 10
Ti	112.82 ± 0.9	Si ₂	139. ± 12
Zr	142.5 ± 0.5	Si ₃	144. ± 15
V	122.7 ± 0.4	Si ₄	153. ± 20
Nb	177 ± 20	Ge	92. ± 3
Ta	185.5 ± 0.3	Ge ₂	109. ± 6
Cr	94.6 ± 1	Ge ₃	120 ± 7
Mo	155.95 ± 0.2	Ge ₄	122 ± 10
W	192.3 ± 1	Ge ₅	138 ± 20
U	116.2 ± 0.2		

Table 1

(Page 2)

Heats of Sublimation of Elemental Species at 298°K

	ΔH_{298} in kcals./mole	ΔH_{298} in kcals./mole	
Ge ₆	140 ± 20	Sb	63. ± 7
Sn	72. ± 0.8	Sb ₂	56. ± 4
Sn ₂	87 ± 5	Sb ₄	48. ± 1
Sn ₃	97 ± 7	Bi	50.0 ± 1
Sn ₄	98 ± 10	Bi ₂	53.5 ± 1
Sn ₅	105 ± 15	S	57.5 ± 1
Pb	46.48 ± 1	S ₂	30.8 ± 0.4
Pb ₂	76. ± 7	S ₄	28. ± 1
P	80. ± 10	S ₆	28. ± 1
P ₂	43. ± 1	S ₈	24.39 ± 0.01
P ₄	30.0 ± 0.9	Se	49. ± 0.5
P ₄ red solid	0	Se ₂	33.3 ± 0.5
As ₄	34.5 ± 1	Se ₆	35.6 ± 1
		Te	47. ± 3
		Te ₂	39.5 ± 1
		Po	31.5 ± 1

Table 2

Heats of Formation of Gaseous Halogen Species from Standard States at 298°K

	ΔH_{298} in kcals./mole	ΔH_{298} in kcals./mole	
F ₂	0.00	Br ₂	7.34 ± 0.05
F	21.15 ± 0.25	Br	26.73 ± 0.04
Cl ₂	0.00	I ₂	14.88 ± 0.005
Cl	28.94 ± 0.03	I	25.49 ± 0.005