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Thermodynamic Data for Synthetic Dawsonite

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THERMODYNAMIC DATA FOR SYNTHETIC DAWSONITE

by

M. J. Ferrante,[1] J. M. Stuve,[1] and D. W. Richardson[2]

ABSTRACT

The standard enthalpy of formation, low-temperature heat capacities, and enthalpy increments above 298 K were determined by the Federal Bureau of Mines for synthetic dawsonite [$NaAlCO_3(OH)_2$]. The enthalpy of formation was determined by hydrochloric acid solution calorimetry, with the result ΔHf°_{298} = -469.4±0.7 kcal/mole. The low-temperature heat capacities were determined from 6 to 307 K by adiabatic calorimetry. Tabulated are low-temperature values of Cp°, S°, and $H.-H^\circ_0$ from 3 to 298 K. The derived entropy at 298 K is S°_{298} = 31.55±0.3 cal/deg mole. Enthalpy increments above 298 K were obtained by copper-block drop calorimetry. Tabular data of Cp°, S°, $H^\circ-H^\circ_{298}$, $-(G^\circ-H^\circ_{298})/T$, ΔHf°, ΔGf°, and log Kf are given from 298 to 477 K. Enthalpies and Gibbs energies of decomposition are also reported.

INTRODUCTION

The mineral dawsonite, which accompanies some extensive oil shale deposits, is a potential source of aluminum. The present calorimetric studies were undertaken to determine its thermodynamic properties.

Included in this Bureau of Mines report are the results of experimental investigations providing the standard enthalpy of formation, low-temperature heat capacities, and enthalpy increments above 298 K. By combining the three experimental investigations, enthalpies of formation and Gibbs energies of formation were calculated from 298 to 477 K. No similar data have appeared in the literature.

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MATERIALS

The dawsonite was synthesized by the procedure described by Jackson (8).[3] The X-ray diffraction pattern of the well-crystallized material was identical to the one published by Jackson who found the unit cell parameters of synthetic dawsonite to be in close agreement with those of a natural mineral.

A chemical analysis performed by this laboratory of material heated to 110° C gave 33.52 pct Al_2O_3, 23.26 pct Na_2O, and 30.13 pct CO_2. The H_2O content of 13.09 pct was obtained by difference from 100 pct. The theoretical amounts are 35.40 pct Al_2O_3, 21.52 pct Na_2O, 30.56 pct CO_2, and 12.51 pct H_2O. Spectrographic analysis showed other compounds to be present in negligible amounts. The chemical analysis corresponds to the composition

$$NaAlCO_3(OH)_2 \cdot 0.0412Na_2CO_3 \cdot 0.0591NaOH \cdot 0.0756H_2O.$$

For calorimetric purposes, the substance was considered to be a mixture of dawsonite and impurity components as given by the preceding formula. Corrections of the measurements that follow were made on this basis.

Other substances used in the enthalpy of formation investigation were reagent-grade materials that were used without correction for impurities.

EXPERIMENTAL WORK AND RESULTS

Enthalpy of Formation

The solution calorimeter employed and its method of operation were described by Mrazek (13). In this instance, the operation was changed slightly so that carbon dioxide could be introduced into the reaction solution. The solution was saturated with CO_2 prior to each determination, and a CO_2 atmosphere was maintained above the solution during the entire period of measurement.

The solution medium was 2131.1 g of hydrochloric acid solution having the composition $HCl \cdot 12.731H_2O$. All measured heat values in this and following sections are expressed in terms of the thermochemical calorie (1 cal = 4.184 J). Atomic weights were taken from the 1971 table of atomic weights (7).

Precision uncertainties of the solution measurements are given as twice the standard deviation of the mean. Absolute uncertainties include, in addition to the precision uncertainties, uncertainties associated with instrumentation, energy calibrations, impurity corrections, carbon dioxide evolution, and supplementary thermodynamic data from the literature. When the heats of two or more reactions were combined, the uncertainty was taken as the square root of the sum of the squares of the absolute uncertainties for the individual reactions.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The reaction scheme used for obtaining the enthalpy of formation of dawsonite is given in table 1. The symbols s, l, g, and sol denote substances that are crystalline, liquid, gaseous, and in solution, respectively. The uncertainties given in table 1 are absolute uncertainties.

TABLE 1. - Calorimetric reaction scheme

Reaction	ΔH_{298}, kcal	Uncertainty, ± kcal
(1) $21.462H_2O(l) = 21.462H_2O(sol)$	-1.71	0.05
(2) $AlCl_3 \cdot 6H_2O(l) = Al^{+3}(sol) + 3Cl^-(sol)$ $+ 6H_2O(sol)$	-7.67	.03
(3) $Na_2CO_3(s) + 2H^+(sol) = 2Na^+(sol)$ $+ H_2O(sol) + CO_2(g)$	-9.91	.03
(4) $2[HCl \cdot 12.731H_2O](l) = 2H^+(sol)$ $+ 2Cl^-(sol) + 25.462H_2O(sol)$	-.01	.01
(5) $NaCl(s) = Na^+(sol) + Cl^-(sol)$	1.92	.04
(6) $NaAlCO_3(OH)_2(s) + 4H^+(sol) = Na^+(sol)$ $+ Al^{+3}(sol) + 3H_2O(sol) + CO_2(g)$	-16.13	.5

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 - \Delta H_6$$

(7) $AlCl_3 \cdot 6H_2O(s) + Na_2CO_3(s) + 21.462H_2O(l)$
$= 2[HCl \cdot 12.731H_2O](l) + NaCl(s) + NaAlCO_3(OH)_2(s)$

$$\Delta H_{298} = -5.1 \pm 0.5 \text{ kcal}$$

A weight of 1.440 g of dawsonite (0.01 mole) served as a basis for the solution measurements. The other substances in the scheme conformed stoichiometrically with this quantity. The heat values and absolute uncertainties for the reaction steps are given in table 1.

Reaction 1 represents the solution of $H_2O(l)$ in the hydrochloric acid solution presaturated with $CO_2(g)$. Six measurements gave -0.0797, -0.0827, -0.0809, -0.0805, -0.0759, and -0.0794 kcal/mole. The mean is -0.0798±0.0018 kcal/mole. The uncertainty given here and for the following solution steps are precision uncertainties.

Reaction 2, the solution of $AlCl_3 \cdot 6H_2O(s)$, was made in the solution resulting from reaction 1. The heats were -7.70, -7.65, -7.69, -7.63, -7.67, and -7.68 kcal/mole. The mean is -7.67±0.02 kcal/mole.

Reaction 3 represents the solution of $Na_2CO_3(s)$ in the solution resulting from reaction 2. The six heats determined were -9.82, -9.85, -9.99, -9.86, -10.00, and -9.95 kcal/mole. The mean is -9.91±0.02 kcal/mole.

In reaction 4, $HCl\cdot 12.731H_2O(l)$ was dissolved in acid solvent of identical composition except for presaturation with $CO_2(g)$. Two determinations gave 0 and -0.010 kcal/mole. The mean is -0.005±0.005 kcal/mole.

Reaction 5, the solution of $NaCl(s)$, was made in the solution resulting from reaction 4. The seven experimental heat values were 1.874, 1.984, 1.902, 1.900, 1.901, 1.911, and 1.955 kcal/mole. The mean is 1.918±0.029.

Finally, the solution of dawsonite (reaction 6) was made in the solution formed after conducting reaction 5. The heats of solution for reaction 6 are -16.27, -15.99, -16.49, -15.83, -16.22, -16.01, and -16.10 kcal/mole. The mean value is -16.13±0.16 kcal/mole. This heat includes impurity corrections, which will be discussed later.

Reactions 3 and 6 would have greater negative values if the carbon dioxide gas released during solution did not cool the solution through vaporization of water. However, since the amount of CO_2 is equal in each case, the calorimetric summation according to table 1 brings about a cancelation of this effect. The heats for reactions 3 and 6 are, therefore, uncorrected for CO_2 evolution.

There remain the corrections for Na_2CO_3, NaOH, and H_2O impurities in the dawsonite, according to the composition $NaAlCO_3(OH)_2\cdot 0.0412Na_2CO_3\cdot 0.0591NaOH\cdot 0.0756H_2O$. The correction for Na_2CO_3 impurity is given by reaction 3 plus a correction for CO_2 evolution. Taking the water vaporization heat to be 0.27 kcal/mole of CO_2 evolved as given by Richardson and Brown (15), the corrected heat for reaction 3 becomes -10.18 kcal/mole of Na_2CO_3. The heat of solution of the Na_2CO_3 impurity per gram formula weight of sample then is 0.0412 × 10.18 = -0.42 kcal.

The correction for NaOH impurity is obtained by the combination of heats for reactions 8 to 11.

$$NaOH(s) + HCl\cdot 12.731H_2O(l) = NaCl(s) + 13.731H_2O(l) \qquad (8)$$

$$13.731H_2O(l) = 13.731H_2O(sol) \qquad (9)$$

$$NaCl(s) = NaCl(sol)$$

$$NaOH(s) + HCl\cdot 12.731H_2O(l) = NaCl(sol) + 13.721H_2O(sol) \qquad (11)$$

$$\Delta H_{11} = \Delta H_8 + \Delta H_9 + \Delta H_{10}$$

To obtain this correction, enthalpy of formation data for $NaOH(s)$, $HCl\cdot 12.731H_2O(l)$, and $H_2O(l)$ were taken from the compilation of Wagman (17). The enthalpy of formation of $NcCl(s)$ was taken from the JANAF tables (3). Table 2 lists the values for these supplementary standard enthalpies of formation. In the case of the solution $HCl\cdot 12.731H_2O(l)$, the enthalpy of formation as given in table 2 is for the reaction

$$1/2H_2(g) + 1/2Cl_2(g) + 12.731H_2O(l) = HCl\cdot 12.731H_2O(l). \qquad (12)$$

Other formations in table 2 are referred to the elements. Reactions 9 and 10 are the same as the measured reactions 1 and 5 in table 1. Combination of the heats of reactions 8 to 10 gives

$$\Delta H_{11} = -25.2 \text{ kcal.}$$

When multiplied by 0.0591, the heat of solution of the NaOH impurity in dawsonite becomes -1.49 kcal/g formula weight of sample.

TABLE 2. - <u>Supplementary formation data</u>

Substance	ΔHf°_{298}, kcal	Reference
$AlCl_3 \cdot 6H_2O(s)$....................	-643.2 ±0.3	1
$Na_2CO_3(s)$........................	-270.26 ± .05	3
$NaCl(s)$..........................	-98.26 ± .08	3
$HCl \cdot 12.731H_2O(l)$.................	-38.82 ± .05	17
$H_2O(l)$..........................	-68.315± .01	17
$NaOH(s)$..........................	-101.72 ± .20	17

The heat of solution of the excess water was estimated to be 3 kcal/mole of H_2O or 0.23 kcal for the 0.0756 mole contained in the gram formula weight.

The mean heat of solution of the uncorrected dawsonite is -17.81 kcal/g formula weight. The summation of the three corrections given above is 1.68 kcal/g formula weight. The difference gives -16.13 kcal/mole of stoichiometric dawsonite. This value appears in table 1 as the heat accompanying reaction 6. The assigned absolute uncertainty of 0.5 kcal/mole contains an allowance for the impurity corrections.

Combination of reactions 1-6 as shown in table 1 gives the enthalpy for calorimetric reaction 7,

$$\Delta H_7 = -5.1 \pm 0.5 \text{ kcal.}$$

Calculation of the standard enthalpy of formation of dawsonite requires supplementary formation data. Combination of ΔH_7 with the supplementary data in table 2 gives

$$\Delta H^{\circ}_{298} = -469.4 \pm 0.7 \text{ kcal/mole}$$

as the standard enthalpy of formation of dawsonite.

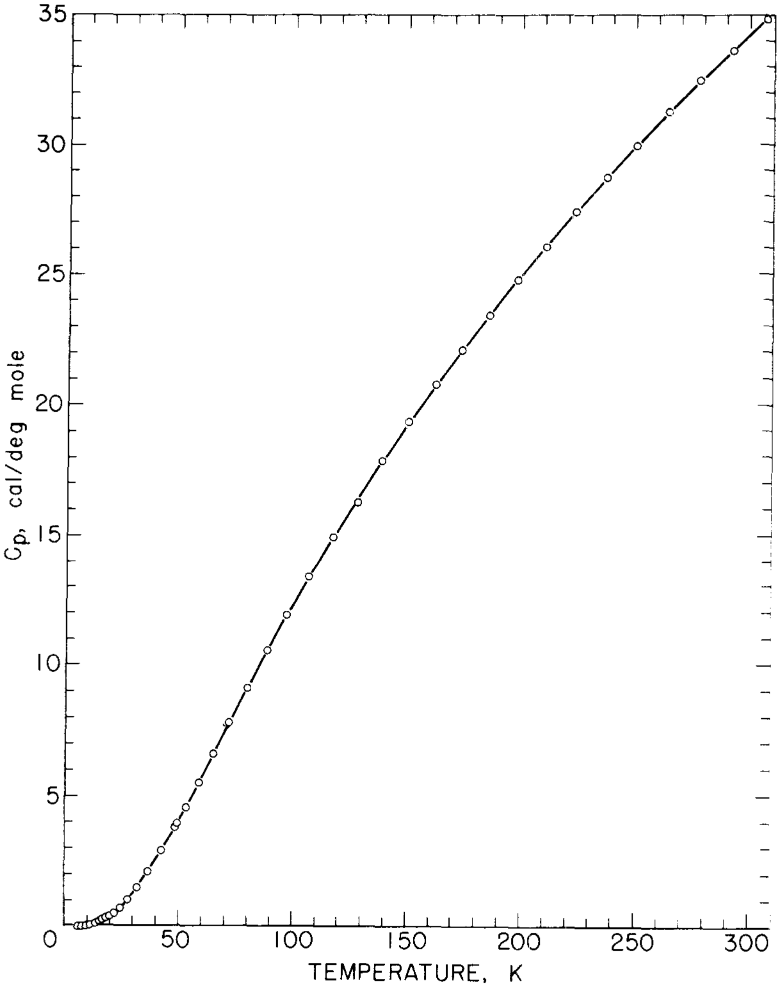

FIGURE 1. - Low-temperature heat capacity.

Low-Temperature Heat Capacities

Low-temperature heat-capacity determinations were made from 6 to 307 K using an adiabatic calorimeter. A detailed description of the calorimeter and its method of operation were reported earlier by Stuve (16). The overall accuracy of the heat capacity values is estimated to be ±1 pct below 25 K; ±0.5 pct, from 25 to 50 K; and 0.2 pct, from 50 to 300 K.

The experimental heat capacities, determined for a sample weight of 45.589 g, are listed in table 3 and plotted in figure 1. The data correspond to the stoichiometric composition, $NaAlCO_3(OH)_2$. Heat-capacity corrections were made for the excess amounts of Na_2CO_3, NaOH, and H_2O. For correction purposes, these excess components (discussed earlier) were treated additively as a mixture. Excess H_2O was considered as ice. The data for these corrections were taken from the compilation of Kelley (10).

Polynomial equations were derived from a least-squares fit of the experimental heat-capacity data by use of a digital computer. Extrapolation of the data from 6 to zero K was made by first graphically fitting the function Cp/T versus T^2, using experimental data between 6.09 and 15.17 K.

Smooth values of heat capacity thus obtained, together with the derived functions of entropy and enthalpy, appear in table 4.

TABLE 3. - Experimental low-temperature heat capacities

T, K	Cp, cal/deg mole	T, K	Cp, cal/deg mole
6.09	0.008	65.04	6.590
7.45	.015	72.05	7.773
8.52	.024	79.89	9.142
9.49	.035	88.59	10.55
10.39	.048	97.02	11.90
11.31	.063	106.69	13.37
12.35	.090	117.34	14.95
13.70	.127	127.89	16.25
15.17	.176	138.80	17.85
16.63	.232	150.30	19.36
18.19	.308	162.24	20.79
19.78	.389	173.83	22.12
21.73	.512	185.72	23.44
24.44	.722	198.24	24.77
27.76	1.034	210.61	26.05
31.75	1.485	223.94	27.40
36.64	2.101	237.36	28.73
42.41	2.907	250.46	29.97
48.41	3.783	264.28	31.25
49.29	3.927	278.18	32.44
53.37	4.554	292.46	33.59
58.79	5.482	307.33	34.81

TABLE 4. - Thermodynamic properties below 298.15 K

T, K	Cal/deg mole		Cal/mole,	T, K	Cal/deg mole		Cal/mole,
	C_p°	S°	$H^\circ - H^\circ_0$		C_p°	S°	$H^\circ - H^\circ_0$
0	0	0	0	140	17.98	12.17	1,085
5	(.005)	(.002)	(.006)	150	19.25	13.45	1,271
10	.041	.013	.100	160	20.47	14.73	1,469
15	.152	.049	.555	170	21.66	16.01	1,680
20	.415	.124	1.904	180	22.81	17.28	1,902
25	.798	.256	4.890	190	23.92	18.54	2,136
30	1.287	.443	10.06	200	24.98	19.80	2,381
35	1.870	.684	17.92	210	26.01	21.04	2,636
40	2.533	.976	28.89	220	27.01	22.27	2,901
45	3.261	1.316	43.35	230	27.99	23.50	3,176
50	4.041	1.700	61.59	240	28.95	24.71	3,461
60	5.703	2.582	110.2	250	29.90	25.91	3,755
70	7.422	3.590	175.8	260	30.84	27.10	4,058
80	9.132	4.693	258.6	270	31.75	28.28	4,371
90	10.79	5.865	358.3	273.15	32.03	28.65	4,472
100	12.37	7.084	474.2	280	32.62	29.45	4,693
110	13.87	8.334	605.4	290	33.45	30.61	5,024
120	15.30	9.603	751.4	298.15	34.08	31.55	5,299
130	16.67	10.88	911.3				

NOTE.--Values in parentheses are extrapolations.

Enthalpies Above 298.15 K

Enthalpy determinations relative to 298.15 K were made with a copper-block drop calorimeter previously described by Douglas (2). The calorimeter was calibrated electrically, and the entire apparatus was checked by determining the enthalpy of pure magnesium oxide (periclase). The 11.130-g sample of dawsonite was enclosed in a platinum-rhodium capsule that was sealed gastight by platinum welding. The relative enthalpies of the empty capsules were determined in separate experiments.

The four experimentally determined enthalpy values are listed in table 5. Enthalpy corrections were made for the excess amounts of Na_2CO_3, NaOH, and H_2O. In this case, the water was treated as combined water. The brucite [$Mg(OH)_2$] data of King (11) were used as a basis for determining the enthalpy of combined water. Other correction data were from the compilation of Kelley (9).

Determinations were stopped when it became apparent that the last valid experimental run was at 477 K. A run at 525 K showed by the thermal effect that a significant change in structure had occurred. The change was known to be irreversible when it was found to be no longer possible to reproduce enthalpy values previously obtained at the lower temperatures. It was, therefore, concluded that decomposition was beginning to occur between 477 and 525 K. This conclusion is in agreement with Harris (4) who determined by X-ray diffraction analysis that the dawsonite structure begins to collapse at 473 K (200° C).

The enthalpy data, plotted in figure 2 as the function $(H-H_{298.15})/(T-298.15)$, gave smooth continuity with the low-temperature heat-capacity data. Although continuity was established down to 260 K, only the 300 K low-temperature value appears in figure 2.

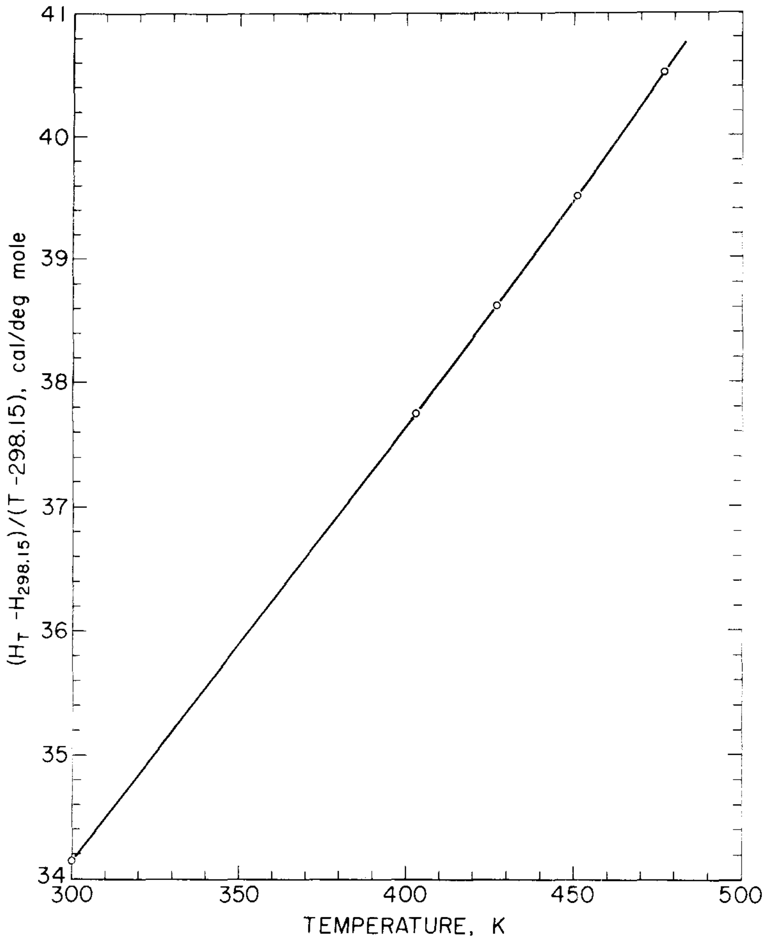

FIGURE 2. - High-temperature enthalpy function.

TABLE 5. - Experimental enthalpies above 298.15 K

T, K	$H^\circ - H^\circ_{298.15}$, cal/mole
402.9	3,953
426.8	4,966
450.9	6,031
477.0	7.241

A polynomial equation was fitted to the experimental enthalpy data. The standard error of the enthalpy values was less than 0.1 pct, and the absolute uncertainty was estimated to be 0.5 pct. The polynomial function was used in combination with the low-temperature data to calculate values of $H^\circ - H^\circ_{292}$, Cp°, S°, and $-(G^\circ - H^\circ_{298})/T$ at intervals of 25°. These properties are listed in table 6. The properties at 298.15 K were taken from the low-temperature data given in table 4.

TABLE 6. - Thermodynamic properties above 298.15 K

T, K	Cal/deg mole			Kcal/mole, $H^\circ - H^\circ_{298}$
	Cp°	S°	$-(G^\circ - H^\circ_{298})/T$	
298.15	34.08	31.55	31.55	0
300	34.22	31.76	31.55	.063
325	35.98	34.57	31.68	.940
350	37.70	37.30	31.98	1.862
375	39.43	39.96	32.42	2.826
400	41.22	42.56	32.98	3.834
425	43.12	45.11	33.61	4.888
450	45.15	47.63	34.32	5.991
475	47.33	50.13	35.09	7.146
477	47.51	50.33	35.15	7.241

The following equation of the form suggested by Maier (12) was derived to fit the $H^\circ - H^\circ_{298}$ data given in table 6.

$$H^\circ - H^\circ_{298.15} = 8.223 \times 10^{-3} T + 3.9997 \times 10^{-5} T^2 - 1.784 \times 10^2 T^{-1} - 5.409. \qquad (13)$$

This equation, expressed in kilocalories per mole, agrees with the tabular data within an average of 0.1 pct.

Enthalpy and Gibbs Energy of Formation and Decomposition

Results from the three experimental investigations (formation, low temperature, and high temperature) may be combined to give enthalpies, Gibbs energies, and equilibrium constants for the formation of dawsonite as a function of temperature. These are listed in tables 7 and 8 for the reactions

$$\mathrm{Na(s,l) + Al(s) + C(graphite) + 5/2O_2(g) + H_2(g) = NaAlCO_3(OH)_2(s)} \quad (14)$$

and $$\mathrm{1/2Na_2O(s) + 1/2Al_2O_3(s) + CO_2(g) + H_2O(l,g) = NaAlCO_3(OH)_2(s).} \quad (15)$$

TABLE 7. - Thermodynamic data for the reaction, $\mathrm{Na(s,l) + Al(s) + C(graphite) + 5/2O_2(g) + H_2(g) = NaAlCO_3(OH)_2(s)}$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔHf°	ΔGf°			ΔHf°	ΔGf°	
298.15	-469.4	-426.9	312.93	375	-470.3	-415.9	242.39
300	-469.4	-426.6	310.78	400	-470.3	-412.3	225.27
325	-469.5	-423.1	284.52	425	-470.3	-408.7	210.17
350	-469.6	-419.5	261.95	450	-470.2	-405.0	196.69
371	-469.7	-416.5	245.35	475	-470.1	-401.4	184.69
371	-470.3	-416.5	245.35	477	-470.1	-401.1	183.77

Phase change: 371 K, melting point of Na; H = 0.621 kcal/mole.

TABLE 8. - Thermodynamic data for the reaction, $\mathrm{1/2\ Na_2O(s) + 1/2Al_2O_3(\alpha) + CO_2(g) + H_2O(g) = NaAlCO_3(OH)_2(s)}$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
0	-65.7	-65.7	∞	375	-67.7	-37.9	22.09
100	-66.9	-59.5	130.04	400	-67.6	-35.9	19.61
200	-67.5	-51.8	56.60	425	-67.6	-33.9	17.43
298.15	-67.7	-44.0	32.25	450	-67.5	-31.9	15.49
300	-67.7	-43.8	31.91	475	-67.3	-29.9	13.76
325	-67.7	-41.8	28.11	477	-67.3	-29.8	13.65
350	-67.7	-39.8	24.85				

In these calculations, supplementary enthalpy and entropy data for sodium and aluminum were taken from Hultgren (6). The standard enthalpy of formation of sodium oxide was from O'Hare (14). All other necessary supplementary data were from the JANAF tables (3).

The thermal decomposition of dawsonite results in the formation of sodium aluminate by the reaction

$$\mathrm{NaAlCO_3(OH)_2(s) = NaAlO_2(s) + CO_2(g) + H_2O(g).} \quad (16)$$

Table 9 gives the enthalpy change, Gibbs energy change, and equilibrium constant for reaction 15 up to 700 K. For these calculations, the present enthalpy data were extrapolated from 477 to 700 K. According to the data in table 9, sodium aluminate becomes thermodynamically stable under 1 atmosphere pressure of decomposition above about 560 K.

TABLE 9. - Thermodynamic data for the reaction, $NaAlCO_3(OH)_2(s) = NaAlO_2(s) + CO_2(g) + H_2O(g)$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
298.15	46.7	22.4	-16.42	500	46.0	6.1	-2.67
300	46.7	22.3	-16.25	550	45.5	2.1	-.83
350	46.7	18.2	-11.36	600	44.9	-1.8	.66
400	46.6	14.1	-7.70	650	44.1	-5.7	1.92
450	46.4	10.1	-4.91	700	43.2	-9.5	2.97

Although thermodynamically correct, reaction 16 is reported in the literature to occur rapidly as the overall reaction only when dawsonite is heated to a temperature in excess of 770 K. Crystalline $NaAlO_2$ is then formed. Below this temperature, the solid products are amorphous. According to Huggins (5), the decomposition takes place in two steps as follows:

$$NaAlCO_3(OH)_2(s) = 1/2Na_2CO_3(\text{amorphous}) + 1/2Al_2O_3(\text{amorphous}) + H_2O(g) + 1/2CO_2(g) \qquad (17)$$

and

$$1/2Na_2CO_3(\text{amorphous}) + 1/2Al_2O_3(\text{amorphous}) = NaAlO_2(\text{crystalline}) + 1/2CO_2(g). \qquad (18)$$

Reaction 17 is reported to start around 500 K, and is complete by about 600 K. Reaction 18 then takes place. Crystalline $NaAlO_2$ begins to form at a temperature variously reported between 770 and 970 K. Because of the amorphous nature of the intermediate products, numerical calculations are not given here for reactions 17 and 18. It can be shown, however, that the decomposition behavior described by earlier workers may be approximated by assuming the intermediate products to be crystalline sodium carbonate and gamma alumina.

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