[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Crystalline $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, and $3CaO \cdot Al_2O_3$

BY JAMES P. COUGHLIN

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Heat of solution measurements of crystalline $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $3CaO \cdot Al_2O_3$, Al and CaO and liquid water were conducted at 303.15°K. in 4.360 *m* hydrochloric acid solution. Based upon these data the following heats of formation from the component oxides at 298.15°K. were derived: $CaO \cdot Al_2O_3$, −3690 ± 350 cal./mole; $12CaO \cdot 7Al_2O_3$, −2710 ± 380 cal. (for $^1/_7$ mole); and $3CaO \cdot Al_2O_3$, −1590 ± 330 cal./mole.

The compounds in the system calcium oxide–aluminum oxide are of interest because of their connection with processes that have been proposed for recovering alumina from siliceous materials (such as clay and anorthosite) and because they are ingredients of Portland cement. The lack of adequate data has prevented detailed thermodynamic consideration of possible reactions involving these compounds. As a step toward alleviating this difficulty, this paper reports the heats of formation of three members of the calcium aluminate series, $3CaO \cdot Al_2O_3(c)$, $12CaO \cdot 7Al_2O_3(c)$ and $CaO \cdot Al_2O_3(c)$. Low temperature heat capacities[1] and high temperature heat contents[2] of these compounds have been reported previously.

Materials

The calcium aluminates $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$ (sample A), and $3CaO \cdot Al_2O_3$ were prepared by prolonged heating of powdered stoichiometric mixtures of reagent grade calcium carbonate and hydrated aluminum oxide (which had been obtained from reagent grade aluminum chloride). These compounds were portions of the samples used by King.[1] X-Ray diffraction data are cited in his paper. The analyses are the same as those reported by him except for atmospheric moisture picked up by the finely ground samples during the process of filling and weighing the sample bulbs.

A new sample of $12CaO \cdot 7Al_2O_3$ (sample B) of somewhat higher purity was prepared by K. C. Conway of this Laboratory especially for this work. His analysis showed 51.48% alumina and 48.42% calcium oxide on an ignited basis, as compared with the theoretical composition 51.47 and 48.53%, respectively. A 95% ethyl alcohol extract of the powdered sample tested colorless to phenolphthalein, thus indicating the absence of free CaO. The X-ray diffraction pattern agreed with that for sample A and with that of Brownmiller and Bogue.[3]

The substance $12CaO \cdot 7Al_2O_3$ presented considerable analytical difficulties concerning its water content. After grinding sample A to −300 mesh for the heat of solution measurements, it contained 1.27% water, of which only 0.03% was lost during a one hour ignition at 1000°. It was found necessary to ignite the sample at a temperature above its melting point,[4] 1450°, for one hour to remove the water completely.

Calcium oxide was made by igniting special reagent grade calcium carbonate (low in alkalies) to constant weight at 1200°. The principal impurity remaining after this treatment was less than 0.3% magnesium oxide. As the heat of solution of magnesium oxide, calculated from data in NBS Circular 500[4] was only 2.3% different from that of calcium oxide on a gram basis, the net correction for this impurity amounted to less than 0.01% and was omitted.

The aluminum metal was in the form of very thin lathe cuttings from two high purity samples furnished by T. H. Hazlett, Division of Mineral Technology, University of California. Analyses furnished with the samples indicated purities of 99.995 and 99.998%. Potassium thiocyanate colorimetric tests for iron indicated less than 0.001% contamination by the lathe cutting tool.

The 4.360 *m* hydrochloric acid was made by diluting reagent grade 37.5% acid with distilled water in batches of about 45 l. each. Each batch was adjusted and standardized to 4.360 ± 0.002 molal against sodium carbonate prepared by decomposing reagent grade sodium bicarbonate to constant weight at 290°. Accurately weighed samples of acid in approximately 0.1% excess were treated with weighed samples of sodium carbonate, boiled, cooled and titrated with 0.05 *N* carbonate-free sodium hydroxide solution to the phenolphthalein end-point.

Thermal corrections for sample impurities are discussed in the next section.

Method and Results

The apparatus employed in all heat of solution measurements was that described by Southard[5] with minor modifications reported by the author in an earlier paper.[6] The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), and all molecular weights were based on the 1953 International Atomic Weights.[7] Sample weights were corrected to vacuum using the following densities: Al, 2.70; CaO, 3.32; H_2O, 0.997; $CaO \cdot Al_2O_3$, 2.98; $12CaO \cdot 7Al_2O_3$, 2.87; $3CaO \cdot Al_2O_3$, 3.0; and 4.360 *m* HCl, 1.062.

In all heat of solution measurements 1,936.2 g. of 4.360 *m* hydrochloric acid was employed as the solvent. The amounts of samples employed were 0.5396 g. of aluminum metal (0.02 mole) and equivalent amounts of all other materials, as they appear below in reactions 5, 12 and 20. By measuring the heat capacity of the calorimeter system both before and after each heat of solution measurement, the ΔC_p of reaction was determined. These data were used when needed to correct the measured heats of reaction to exactly 30.00°; most of the measurements were made within 0.01 of 30.00° and required no correction.

Because the electrical calibration measurements were made at lower temperatures than the corresponding heat of solution measurements, a small correction was applied to each solution result. This correction amounted to −54 cal./mole for the aluminum measurements, −24 cal./mole for the $CaO \cdot Al_2O_3$ measurements, −0.17 cal./g. for the $12CaO \cdot 7Al_2O_3$ measurements and −70 cal./mole for the $3CaO \cdot Al_2O_3$ measurements. For the calcium oxide measurements this correction varied from −6 to −13 cal./mole, depending upon sample size.

The measurements of two of the substances include corrections for water impurity based on an assumed binding energy of 79.70 cal./g., equal to the heat of fusion of ice. The net corrections were −116 and −150 cal./mole for the $CaO \cdot Al_2O_3$ samples containing 0.10 and 0.13%, respectively, and −175 cal./mole for the $3CaO \cdot Al_2O_3$ sample which contained 0.08% water. Corrections for the water impurity in the calcium oxide samples were based on the heat of hydration measurements of Taylor and Wells.[8] This correction was −105 cal./mole for 0.11% water (or 0.45% calcium hydroxide). All other experimental corrections are discussed in connection with the individual sets of measurements.

In the calculations and discussion that follow, several data are taken from the literature. Values for heat capacities

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[1] E. G. King, *J. Phys. Chem.*, **59**, 218 (1955).

[2] K. R. Bonnickson, *ibid.*, **59**, 220 (1955).

[3] L. T. Brownmiller and R. H. Bogue, *Amer. J. Sci.*, **23**, 508 (1932).

[4] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circular 500, 1952.

[5] J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[6] J. P. Coughlin, THIS JOURNAL, **77**, 868 (1955).

[7] E. Wichers, *ibid.*, **76**, 2033 (1954).

[8] K. Taylor and L. S. Wells, *J. Research Natl. Bur. Standards*, **21**, 133 (1938).

TABLE I

HEAT OF FORMATION OF $CaO\cdot Al_2O_3$ (CAL./MOLE) (Mol. wt. = 158.04)

Reaction		$\Delta H_{303.15}$	Uncertainty
$2Al(c) + 6H^+(sol) = 2Al^{+++}(sol) + 3H_2(g)$	(1)	−254,100	±240
$CaO(c) + 2H^+(sol) = Ca^{++}(sol) + H_2O(sol)$	(2)	− 47,440	± 30
$3H_2O(l) = 3H_2O(sol)$	(3)	−250	± 10
$CaO\cdot Al_2O_3(c) + 8H^+(sol) = Ca^{++}(sol) + 2Al^{+++}(sol) + 4H_2O(sol)$	(4)	−102,420	±150
$2Al(c) + CaO(c) + 3H_2O(l) = CaO\cdot Al_2O_3(c) + 3H_2(g)$	(5)	−199,370	±290

At 298.15°K., $\Delta H_5 = -199{,}370 + 130 = -199{,}240 \pm 290$

and entropies at 298.15°K. are taken from the compilation of Kelley[9] and from papers by King[1] and Kerr, Johnston and Hallett.[10] Heats of formation are from Mah[11] and a compilation by the author.[12] High temperature heat content data are from Kelley[13] and Bonnickson.[2]

$CaO\cdot Al_2O_3$.—Table I gives the skeleton equations for the reactions measured to obtain the heat of formation of $CaO\cdot Al_2O_3(c)$.

Reactions 1, 2 and 3 were measured consecutively in the same acid solution. Reaction 4 was measured in a fresh portion of the acid. Thus the final solution from reactions 1, 2 and 3 and the final solution from reaction 4 are identical, and $\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$.

Five measurements were made of the molal heat of solution of aluminum in 4.360 *m* hydrochloric acid, giving −127,050 ± 120 cal./mole as the mean of −126,930, −127,230, −126,930, −127,010 and −127,130. These measurements include a correction of −483 cal./mole for heat absorbed in the vaporization of water and hydrogen chloride by the escaping hydrogen gas. The acid solution was saturated with hydrogen gas before the start of the measurements, to ensure that all of the hydrogen evolved actually left the calorimeter. The correction is based upon the assumption that this gas is saturated with water and hydrogen chloride, whose vapor pressures and heats of vaporization at the mean reaction temperature of 29.25° are 23.2 mm. and 10,500 cal./mole, respectively, for water, and 0.0472 mm. and 16,850 cal./mole, respectively, for hydrogen chloride. The heat evolved in the reduction of the chloroplatinic acid used as a catalyst for the reaction made necessary an additional correction of +7 cal./mole.

Fifteen measurements of the heat of solution of calcium oxide were made in solutions equivalent to the final solution from reaction 1. The samples ranged in size from 0.2707 to 1.5988 g. in order to make the results applicable to all three calcium aluminates. The data are listed in Table II and, within experimental error, show no dependence on sample size.

Table III shows the data used for reaction 3. The measurements were made in acid solutions containing 0.5396 g. of aluminum and various amounts of calcium oxide. The heat of reaction was independent of both the water sample size and the amount of calcium ion in solution. In two of the runs, the water sample size was nearly twice the theoretical sample size (0.5405 g.); this was done merely to improve the accuracy of the measurement.

TABLE II

HEAT OF SOLUTION OF CaO(c) (CAL./MOLE)

Mol. wt. = 56.08

CaO wt., g.	$\Delta H_{303.15}$	CaO wt., g.	$\Delta H_{303.15}$	CaO wt., g.	$\Delta H_{303.15}$
0.7115	−47,474	0.7075	−47,449	1.1211	−47,446
.6958	−47,489	.3772	−47,440	1.3058	−47,403
.7610	−47,510	.2707	−47,389	1.3119	−47,498
.5485	−47,375	.4553	−47,328	1.3537	−47,501
.4894	−47,389	.3532	−47,428	1.5988	−47,491

Mean $\Delta H_{303.15}$ = −47,441 ± 29 cal./mole

TABLE III

HEAT OF SOLUTION OF $H_2O(l)$ (CAL./MOLE)

Mol. wt. = 18.016

H_2O, g.	CaO in soln., g.	$\Delta H_{303.15}$ (cal./mole)
0.5843	0.7075	−80.8
0.5652	0.4678	−84.0
1.0511	0.6958	−80.8
0.9175	1.3537	−84.6

Mean $\Delta H_{303.15}$ = −82.6 ± 2.1 cal./mole

The heat of reaction 4, −102,420 ± 150 cal./mole, was the mean of six measurements, −102,560, −102,230, −102,330, −102,320, −102,700 and −102,380. Five of the measurements were made with a −300 mesh sample; the water content of this sample was 0.10% and the time required for complete solution varied from 132 to 144 min. One measurement was made with an extra finely ground sample; it had a water content of 0.13% and an equilibrium time of 120 min.

Reaction 5 represents the heat of formation of calcium aluminate, $CaO\cdot Al_2O_3$, at 303.15°K. from aluminum metal, calcium oxide and liquid water. The heats of formation from the component oxides, reaction 6, and from the elements, reaction 7, are computed by substitution of literature values[11,12] of the heats of formation of corundum, water and calcium oxide.

$$CaO(c) + Al_2O_3(\alpha) = CaO\cdot Al_2O_3(c) \qquad (6)$$

$$\Delta H_{298.15} = -3{,}690 \pm 350 \text{ cal./mole}$$

$$Ca(c) + 2Al(c) + 2O_2(g) = CaO\cdot Al_2O_3(c) \qquad (7)$$

$$\Delta H_{298.15} = -554{,}840 \pm 500 \text{ cal./mole}$$

$12CaO\cdot 7Al_2O_3$.—Table IV gives the skeleton equations for the reactions studied to obtain the heat of formation of $12CaO\cdot 7Al_2O_3(c)$. For convenience, this compound will be referred to as $12/7CaO\cdot Al_2O_3(c)$, thus allowing intercomparisons of data for the three aluminates on the basis of one mole of alumina.

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(9) K. K. Kelley, U. S. Bur. Mines Bulletin 477, 1950.

(10) E. C. Kerr, H. L. Johnston and N. C. Hallett, THIS JOURNAL, **72**, 4740 (1950).

(11) Heat of formation of Al_2O_3 (α, corundum): $\Delta H_{298.15}$ = −400,500 ± 200 cal./mole. A. D. Mah, unpublished measurements, this Laboratory.

(12) J. P. Coughlin, U. S. Bur. Mines Bulletin 542, 1954.

(13) K. K. Kelley, U. S. Bur. Mines Bulletin 476, 1949.

TABLE IV

HEAT OF FORMATION OF $12/7CaO \cdot Al_2O_3(c)$ (CAL./MOLE) (Mol. wt. = 198.10)

Reaction		$\Delta H_{298.15}$	Uncertainty
$2Al(c) + 6H^+(sol) = 2Al^{+++}(sol) + 3H_2(g)$	(8)	−254,100	±240
$12/7CaO(c) + 24/7H^+(sol) = 12/7Ca^{++}(sol) + 12/7H_2O(sol)$	(9)	− 81,330	± 50
$3H_2O(l) = 3H_2O(sol)$	(10)	−250	± 10
$12/7CaO \cdot Al_2O_3(c) + 66/7H^+(sol) = 12/7Ca^{++}(sol) + 2Al^{+++}(sol) + 33/7H_2O(sol)$	(11)	−137,290	±200
$2Al(c) + 12/7CaO(c) + 3H_2O(l) = 12/7CaO \cdot Al_2O_3(c) + 3H_2(g)$	(12)	−198,390	±320

At 298.15°K., $\Delta H_{12} = -198{,}390 + 130 = -198{,}260 \pm 320$ cal./mole

Reactions 8, 9 and 10 have already been discussed as reactions 1, 2 and 3, respectively; ΔH_9 is merely $12/7\Delta H_2$.

The data for obtaining ΔH_{11} are listed in Table V. The powdered crystalline sample of $12/7CaO \cdot Al_2O_3$ could not be completely dehydrated below its melting point; therefore a series of measurements were made with samples containing various amounts of water, and the data extrapolated to zero water content. The precision uncertainty of the results, based on deviations from the best linear equation (equation 13), is ± 130 cal./mole. The estimated over-all uncertainty of the extrapolated value is ±200 cal./mole.

All measurements with sample A include a net correction of −0.45 cal./g. for 0.10% ferric oxide impurity. The extrapolated value corresponds to −137,290 cal./mole and is based on the assumption that the binding energy of the water impurity in the composition range 0 to 0.41% is equal to that for the composition range 0.41% to 1.31%. If the water below 0.41% is more tightly bound than the average in the measured range, then ΔH_{11} would be more negative and ΔH_{12} would be less negative.

TABLE V

HEAT OF SOLUTION OF $12/7CaO \cdot Al_2O_3 \cdot xH_2O$ (CAL./G.)

Sample	Water content, %	$\Delta H_{303.15}$ (cal./g.)	Sample	Water content, %	$\Delta H_{303.15}$ (cal./g.)
A	1.24	−655.33	B	1.24	−653.11
A	1.27	−654.46	B	0.94	−662.97
A	1.27	−655.03	B	.83	−667.96
A	1.27	−654.98	B	.63	−673.63
A	1.27	−654.61	B	.58	−675.64
A	1.27	−655.18	A	.41	−681.64
B	1.31	−654.79	Extrapolated	0	(−693.02)

ΔH sol. = −693.02 + 30.18 × (H_2O content in %), cal./g. (13)

TABLE VI

HEAT OF FORMATION OF $3CaO \cdot Al_2O_3(c)$ (CAL./MOLE) (Mol. wt. = 270.20)

Reaction		$\Delta H_{303.15}$	Uncertainty
$2Al(c) + 6H^+(sol) = 2Al^{+++}(sol) + 3H_2(g)$	(16)	−254,100	±240
$3CaO(c) + 6H^+(sol) = 3Ca^{++}(sol) + 3H_2(sol)$	(17)	−142,320	± 90
$3H_2O(l) = 3H_2O(sol)$	(18)	−250	± 10
$3CaO \cdot Al_2O_3(c) + 12H^+(sol) = 3Ca^{++}(sol) + 2Al^{+++}(sol) + 6H_2O(sol)$	(19)	−199,400	± 40
$2Al(c) + 3CaO(c) + 3H_2O(l) = 3CaO \cdot Al_2O_3(c) + 3H_2(g)$	(20)	−197,270	±260

At 298.15°K., $\Delta H_{20} = -197{,}270 + 130 = -197{,}140 \pm 260$ cal./mole

Combining equations in a manner similar to that for $CaO \cdot Al_2O_3$, $\Delta H_{12} = \Delta H_8 + \Delta H_9 + \Delta H_{10} - \Delta H_{11}$. The heats of formation from the component oxides, reaction 14, and from the elements, reaction 15, are computed by substitution of appropriate literature values.

$12/7CaO(c) + Al_2O_3(\alpha) = 12/7CaO \cdot Al_2O_3$ (14)

$\Delta H_{298.15} = -2{,}710 \pm 380$ cal./mole

$12/7Ca(c) + 2Al(c) + 33/14O_2 = 12/7CaO \cdot Al_2O_3(c)$ (15)

$\Delta H_{298.15} = -661{,}470 \pm 760$ cal./mole

$3CaO \cdot Al_2O_3(c)$.—Equation 20 in Table VI shows the net reaction investigated to determine the heat of formation of $3CaO \cdot Al_2O_3(c)$.

The heat of solution of $3CaO \cdot Al_2O_3(c)$, reaction 19, is the mean of five measurements, −199,360, −199,440, −199,420, −199,360 and −199,430. Reactions 16, 17 and 18 have been discussed previously as reactions 1, 2 and 3.

Combination of reaction 20 with data from the literature yields the heats of reaction

$3CaO(c) + Al_2O_3(\alpha) = 3CaO \cdot Al_2O_3(c)$ (21)

$\Delta H_{298.15} = -1590 \pm 330$ cal./mole

$3Ca(c) + 2Al(c) + 3O_2(g) = 3CaO \cdot Al_2O_3(c)$ (22)

$\Delta H_{298.15} = -850{,}040 \pm 1{,}230$ cal./mole

Discussion

Thermodynamic consideration of all possible reactions involving the three calcium aluminates, calcium oxide and alumina are entirely consistent with the methods of preparation described by King.[1] The free energy changes involved in direct combinations of the constituent oxides, reactions 6, 14 and 21, are all negative at 298.15° K. (Table VII), and increasingly negative with increasing temperature to the limits of the available data.

The reactions shown in Table VIII indicate that $12/7CaO \cdot Al_2O_3(c)$ and $3CaO \cdot Al_2O_3(c)$ are metastable at room temperature. However $\Delta F°$ of reaction 23 becomes zero at about 580°K. and decreases to a value of −3,160 cal./mole at 1700°K. Similarly, $\Delta F°$ of reaction 24 decreases to zero at about 710°K. and to −3,430 cal./mole at 1800°K. The free energy change of reaction (25) becomes zero at about 1,050°K. and is negative at temperatures between 1,050 and 1,700°K.

Similar combinations of the data from 298.15 to 1800°K. indicate that $CaO \cdot Al_2O_3(c)$ is stable by a wide margin with respect to decomposition into alumina plus an aluminate of higher calcium content ($12/7CaO \cdot Al_2O_3(c)$ or $3CaO \cdot Al_2O_3(c)$). Likewise, $12/7CaO \cdot Al_2O_3(c)$ has great stability with re-

TABLE VII

HEATS AND FREE ENERGIES OF FORMATION (KCAL./MOLE)

Substance	From the oxides		From the elements	
	$\Delta H_{298.15}$	$\Delta F_{298.15}$	$\Delta H_{298.15}$	$\Delta F_{298.15}$
$CaO \cdot Al_2O_3(c)$	−3.69 ± 0.35	−5.36 ± 0.37	−554.8 ± 0.5	−526.8 ± 0.5
$12/7CaO \cdot Al_2O_3(c)$	−2.71 ± .38	−4.86 ± .40	−661.5 ± 0.8	−628.6 ± 0.8
$3CaO \cdot Al_2O_3(c)$	−1.59 ± .33	−4.09 ± .40	−850.0 ± 1.2	−807.9 ± 1.2

TABLE VIII

HEATS AND FREE ENERGIES OF REACTION (CAL./MOLE)

Reaction		$\Delta H_{298.15}$	$\Delta F_{298.15}$
$5/7CaO(c) + CaO \cdot Al_2O_3(c) = 12/7CaO \cdot Al_2O_3(c)$	(23)	+ 980 ± 260	+ 500 ± 270
$2CaO(c) + CaO \cdot Al_2O_3(c) = 3CaO \cdot Al_2O_3(c)$	(24)	+2100 ± 170	+1270 ± 250
$12/7CaO \cdot Al_2O_3(c) + 9/7CaO(c) = 3CaO \cdot Al_2O_3(c)$	(25)	+1120 ± 210	+ 760 ± 260

spect to decomposition into alumina plus tricalcium aluminate.

NOTE ADDED IN PROOF.—Recently E. J. Huber, Jr., and C. E. Holley, Jr., *J. Phys. Chem.*, 60, 498 (1956), have reported new experimental work leading to $\Delta H_{298.15} = -151.79$ kcal./mole as the heat of formation of calcium oxide. As a consequence, the heats and free energies of formation of the calcium aluminates from the elements (reactions 7, 15, and 22 and values in the last two columns of Table VII) should be more negative by 1.14 kcal./mole of calcium. The heats and free energies of formation from the oxides remain unchanged.

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The Freezing Point Method of Determining Free Energies in a 2-Component System Forming Compounds. Concentrated Aqueous Sulfuric Acid[1]

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A method is described in which freezing point observations may be utilized to obtain the partial molal free energies at all concentrations in a two-component liquid in equilibrium with a series of pure compounds. The method is illustrated by the determination of the variation of the free energy of water in aqueous sulfuric acid from $A = 2$ to $A = -0.005$, where A repsents the water in $H_2SO_4 \cdot AH_2O$.

The use of the freezing point method for accurately determining the partial molal free energies in two-component solutions has been essentially restricted to aqueous solutions over the concentration range in which they may be brought into equilibrium with ice. There is a rather widely held feeling, perhaps based on numerous phase diagrams for somewhat similar components, usually metals, at high temperatures, that solid solutions are to be expected in most cases when various solid phases are formed. Many years of experience in calorimetric studies of a wide variety of substances, in this Laboratory, has led us to conclude that ice is not exceptional in its ability to crystallize from a solution in a highly pure state.

The problem of proving that a solid phase is pure is not one that can be solved easily even with the most careful of ordinary analytical procedures because we have at the same time found that it is, for example, extraordinarily difficult to crystallize compounds from water solutions without solution inclusions, "brine holes," within defects. However the heat effects accompanying eutectic melting, and changing solubility with temperature, make such liquid inclusions in crystals very obvious in the course of accurate heat capacity observations.

Theoretically, pure compounds are thermodynamically stable only at the absolute zero, where equilibrium solutions are ruled out in accordance with the third law of thermodynamics, but actually ordinary temperatures are close enough to the absolute zero so that highly pure substances can and usually do form. The existence of the law of simple multiple proportions and the large number of high quality atomic weight determinations based upon it supplies substantial evidence. This is not inconsistent with the fact that thermodynamic considerations make it certain that the equilibrium presence of foreign components in a solid will increase rapidly with increasing high temperatures.

When the freezing point method of determining free energy is used, the presence of solution inclusions in "brine holes" is not important. Such inclusions will come to equilibrium internally and should have no effect on the equilibrium between the pure outer crystalline surface and the solution taken for analysis.

However, even when a series of compounds separate as essentially pure phases there is still a problem in the experimental determination of the continuous free energy relationship over the whole range of concentration. This type of calculation has not previously been discussed.

The Partial Molal Free Energies in Aqueous Sulfuric Acid from the Freezing Point–Composition Data.—The calculation of the change of partial

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