TABLE II

VARIATION OF $E_{1/2}$ WITH pH FOR 10^{-3} M CHLORANILIC ACID
IN BUFFERS OF TOTAL IONIC STRENGTH 1.0

Composition	pH	$E_{1/2}$ vs. S.C.E., v.
$H_2SO_4 + K_2SO_4$	0.40	+0.160
$H_2SO_4 + K_2SO_4$	0.72	+ .145
$H_2SO_4 + K_2SO_4$	1.13	+ .123
$H_2SO_4 + K_2SO_4$	1.53	+ .095
Citric acid + Na_2HPO_4 + $NaNO_3$	2.07	+ .042
Citric acid + Na_2HPO_4 + $NaNO_3$	2.26	+ .024
Citric acid + Na_2HPO_4 + $NaNO_3$	2.50	+ .003
Acetic acid + NaAc + KCl	4.12	− .179
Acetic acid + NaAc	4.67	− .230
Citric acid + Na_2HPO_4 + K_2SO_4	5.12	− .293
Citric acid + Na_2HPO_4 + K_2SO_4	5.98	− .394
Na_2HPO_4 + NaH_2PO_4 + KCl	6.58	− .471
Na_2HPO_4 + NaH_2PO_4 + KCl	6.61	− .468
Na_2HPO_4 + NaH_2PO_4 + KCl	7.11	− .530

TABLE III

PROPORTIONALITY BETWEEN DIFFUSION CURRENT
AND CONCENTRATION

$M \times 10^3$	$C =$ $i_d,$ $\mu a.$	i_d/C	Deviation

In 0.1 N H_2SO_4, with $m^{2/3}t^{1/6} = 1.59$ mg.$^{2/3}$ sec.$^{-1/3}$

2.0	12.75	6.37	−0.08
1.0	6.43	6.43	− .02
0.10	0.645	6.45	.00
.02	.129	6.45	.00
.01	.066	6.55	+ .10
	Av.	6.45	±0.04

In citric acid + Na_2HPO_4 buffer of pH 3.62,
with $m^{2/3}t^{1/6} = 1.68$ mg.$^{2/3}$ sec.$^{-1/3}$

5.0	32.80	6.75	−0.16
2.0	13.37	6.69	− .02
1.0	6.75	6.75	+ .04
0.5	0.342	6.84	+ .13
	Av.	6.71	±0.09

be non-existent, as is shown by the data of Table IV. On the basis of the Ilkovic equation we find that the average diffusion coefficient of the reducible
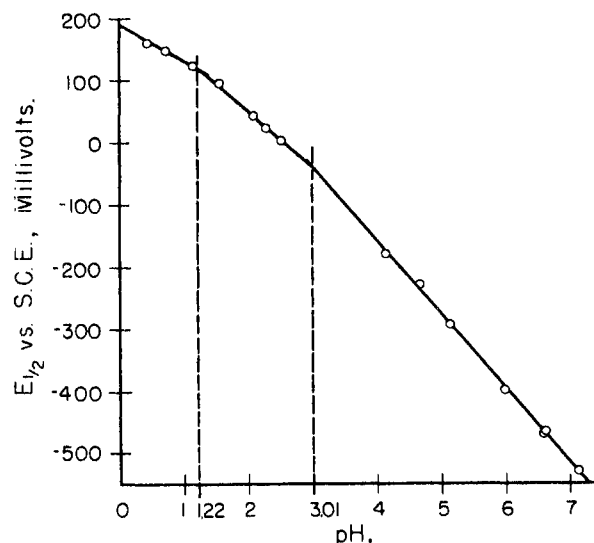

Fig. 1.—Variation of $E_{1/2}$ with pH for 0.001 M chloranilic acid in buffers of ionic strength of 1.0.

TABLE IV

CONSTANCY OF DIFFUSION CURRENT WITH pH FOR 10^{-3} M
CHLORANILIC ACID

pH	$i_d,$ mm.	pH	$i_d,$ mm.
4.32	106	2.44	110
3.89	107	1.82	110
3.48	109	1.70	106
3.30	107	1.23	106
2.88	109	0.91	110
		Av.	108 ± 1.6

species H_2Q, HQ^- and Q^{--} of chloranilic acid is 1.04×10^{-5} cm.^{2} sec.$^{-1}$.

HIGH TEMPERATURE HEAT CONTENTS OF CALCIUM ORTHOSILICATE

By J. P. Coughlin and C. J. O'Brien

Contribution from the Minerals Thermodynamics Experiment Station, Region II, Bureau of Mines, United States Department of the Interior, Berkeley, Cal.

High temperature heat content measurements were made involving four crystalline varieties of calcium orthosilicate. The entropies and heats of the $\beta \rightarrow \alpha'$, $\alpha' \rightarrow \alpha$, and $\gamma \rightarrow \alpha'$ transformations were evaluated. A table of smooth values of heat content and entropy increments above 298.15°K. and algebraic representations of the heat contents are included, for use in thermodynamic calculations.

Introduction.—There are four crystalline varieties of calcium orthosilicate (Ca_2SiO_4) according to the work of Bredig[1] and Trömel and Möller.[2] The designations α, α', β and γ, used by those authors, are adopted here. Two varieties are common at room temperature, β and γ. The β-form is

(1) M. A. Bredig, J. Am. Ceram. Soc., 33, 188 (1950).
(2) G. Trömel and H. Möller, Fortsch. Mineral., 28, 80 (1949).

thermodynamically unstable throughout its temperature range of existence. It transforms at 970°K. into the α'-variety which itself is a metastable modification at this temperature. The γ-variety is the "dusting" form sometimes observed in the manufacture of Portland cement and during cooling of high lime-containing slags. It is the thermodynamically stable form to about 1120°K.
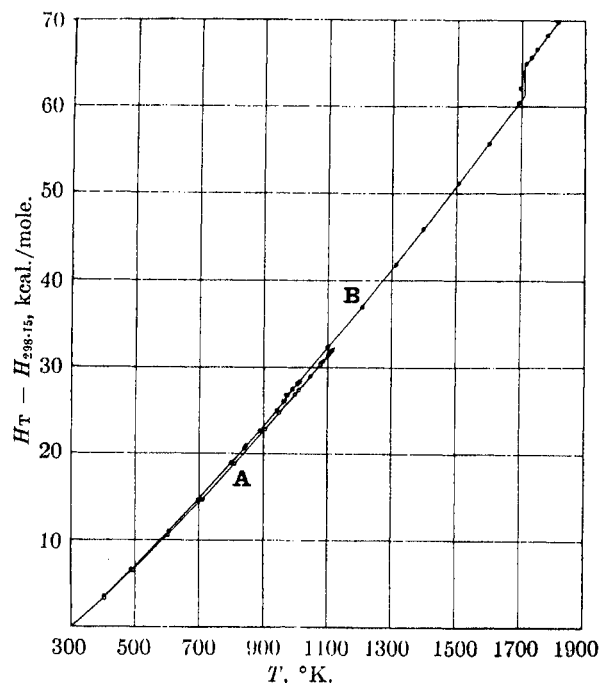
Fig. 1.—Heat contents above 298.15°K.: A, $Ca_2SiO_4(\gamma)$;
B, $Ca_2SiO_4(\beta, \alpha', \alpha)$.

where it transforms into α'. The α'-variety is thermodynamically stable between 1120 and 1710° K. where it, in turn, transforms into α. The α-variety is stable between 1710°K. and the melting point.

The energy relationships among these crystalline varieties have been known only qualitatively and it is the purpose of the present paper to supply some quantitative data. High temperature heat content measurements of the γ-variety have been conducted from 298 to 1113°K. Measurements starting with the β-variety at 298°K. were carried to 1816°K., data being obtained for the β-, α'- and α-varieties and for the transformations $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$. The only previous similar measurements of calcium orthosilicate are those of von Gronow and Schwiete[3] between 293 and 1573°K. Their measurements were made before the inter-relationships among the four varieties were completely unravelled and they leave much to be desired as to accuracy.

Materials.—The β-variety of calcium orthosilicate was part of the sample used by King[4] in heat of formation determinations and by Todd[5] in low temperature heat capacity measurements. The method of preparation, chemical analysis and X-ray diffraction are described by King.[4] The sample contained 64.47% calcium oxide, 34.68% silica, 0.32% aluminum and iron oxides, 0.14 magnesium oxide, and 0.02% water, as compared with the theoretical 65.11% calcium oxide and 34.89 silica.

The γ-variety was prepared from reagent-grade calcium carbonate and silica, using platinum containers. A stoichiometric mixture was made into a paste with water, dried at 1000°, heated 2 hours at 1440°, cooled to 1000° in 1 hour, transferred to a furnace at 500°, and allowed to cool slowly (overnight) to 350°. This process was repeated 4 times, with intervening grinding, mixing, analysis and adjustment of composition. The final product contained 34.88% silica, which is virtually the theoretical amount for pure

(3) H. E. von Gronow and H. E. Schwiete, Z. anorg. Chem., **216**, 185 (1933).

(4) E. G. King, J. Am. Chem. Soc., **73**, 656 (1951).

(5) S. S. Todd, ibid., **73**, 3277 (1951).

calcium orthosilicate. Its X-ray diffraction pattern agreed with that for the γ-variety in the ASTM catalog.

Measurements and Results.—The heat content measurements were conducted with previously described apparatus.[6] Sealed, platinum–rhodium capsules were used to contain the samples during the measurements. The heat contents of the empty capsules were determined in separate experiments. The results for calcium orthosilicate are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole, the molecular weight being 172.25, in accordance with the 1954–55 Report on Atomic Weights.[7] The measured heat contents are listed in Table I and plotted in Fig. 1.

TABLE I

HEAT CONTENTS OF CALCIUM ORTHOSILICATE ABOVE 298.15°K.

$T,°K.$	$H_T - H_{298.15},$ cal./mole	$T,°K.$	$H_T - H_{298.15},$ cal./mole	$T,°K.$	$H_T - H_{298.15},$ cal./mole
		$Ca_2SiO_4(\gamma)$ (mol. wt., 172.25)			
405.2	3,300	948.8	24,700	1079.4	30,490
494.4	6,470	999.1	26,830	1085.3	30,650
602.3	10,570	1008.6	27,280	1100.1	31,270
704.9	14,580	1045.4	28,900	1104.6	31,540
810.5	18,850	1050.8	29,220	1108.3	31,630
905.7	22,800	1075.2	30,270	1112.9	31,820
		Ca_2SiO_4 (β, α', α) (mol. wt., 172.25)			
406.0	3,540	974.1	26,720	1602.3	55,650
489.0	6,530	977.4	26,880	1690.6	60,410
604.9	10,990	990.4	27,430	1697.7	62,130ᵃ
694.2	14,580	1003.8	28,070	1706.7	63,880ᵃ
799.0	18,890	1012.3	28,410	1714.6	64,930
840.0	20,610	1099.1	32,260	1730.5	65,670
847.7	20,930	1206.0	36,910	1747.4	66,620
888.9	22,660	1312.2	41,800	1780.8	68,200
940.8	24,890	1397.3	45,850	1816.0	69,730
964.6	26,000	1506.8	51,100		

ᵃ Shows pretransition effect.

The heat content of the γ-variety follows a regular, reproducible course to about 1120°K., that is, to the temperature of transformation to α'. Reproducible values at higher temperatures could not be obtained because of the sluggishness of the $\alpha' \rightarrow \gamma$ transformation. The substance did not revert completely to the γ-form under the prevailing conditions, resulting in calorimetric end-products of variable crystallographic composition. This behavior is in line with the observations of Trömel and Möller.[2]

Measurements starting with the β-variety were highly reproducible over the entire temperature range from 298 to 1816°K. The $\beta \rightarrow \alpha'$ transformation was sharp and completely reversible under calorimetric conditions. The measurement at 964.6°K. showed no sign of any transformation effect, while that at 974.1°K. showed that complete transformation had occurred. The rounded temperature, 970°K., was adopted as the equilibrium $\beta \rightarrow \alpha'$ point. Likewise, the $\alpha' \rightarrow \alpha$ transformation was completely reversible under calorimetric conditions. Pretransition effects were noted in the measurements at 1697.7 and 1706.7°K., but the transformation was complete at 1714.6°K. The rounded value, 1710°K., was adopted as the equilibrium $\alpha' \rightarrow \alpha$ point.

(6) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(7) E. Wichers, J. Am. Chem. Soc., **78**, 3235 (1956).

Table II contains smooth values of the heat content and entropy increments above 298.15°K. Values in the columns headed "$Ca_2SiO_4(\gamma)$" are based upon the γ-variety as the reference state at 298.15°K. Those in the columns headed "$Ca_2SiO_4(\beta,\alpha',\alpha)$" are based upon the β-variety as the reference state at 298.15°K.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY INCREMENTS (CAL./DEG. MOLE) ABOVE 298.15°K.

T, °K.	Ca₂SiO₄ (γ)		Ca₂SiO₄ (β, α', α)	
	$H_T - H_{298.15}$	$S_T - S_{298.15}$	$H_T - H_{298.15}$	$S_T - S_{298.15}$
400	3,270	9.41	3,335	9.59
500	6,760	17.19	6,940	17.63
600	10,480	23.96	10,790	24.64
700	14,380	29.97	14,810	30.84
800	18,420	35.37	18,940	36.35
900	22,590	40.28	23,140	41.29
970	....	...	26,120(β)	44.48
970	....	...	26,560(α')	44.94
1000	26,890	44.81	27,860	46.26
1100	31,320	49.03	32,250	50.44
1120	32,220	49.84	33,140	51.24
1200			36,720	54.33
1300			41,290	57.99
1400			45,970	61.45
1500			50,780	64.77
1600			55,710	67.95
1700			60,780	71.03
1710			61,290(α')	71.33
1710			64,680(α)	73.31
1800			69,090	75.82

The heat content results in Table II are represented (to within the average deviations indicated

below) by the equations

$Ca_2SiO_4(\gamma)$

$$H_T - H_{298.15} = 31.86T + 6.16 \times 10^{-3}T^2 + 4.64 \times 10^5 T^{-1} - 11,603$$
$$(0.2\%, 298° - 1100°K.)$$

$Ca_2SiO_4(\beta)$

$$H_T - H_{298.15} = 34.87T + 4.87 \times 10^{-3}T^2 + 6.26 \times 10^5 T^{-1} - 12,929$$
$$(0.4\%, 298° - 970°K.)$$

$Ca_2SiO_4(\alpha')$

$$H_T - H_{298.15} = 32.16T + 5.51 \times 10^{-3}T^2 - 9,814$$
$$(0.1\%, 970° - 1710°K.)$$

$Ca_2SiO_4(\alpha)$

$$H_T - H_{298.15} = 49.00T - 19,110$$
$$(0.1\%, 1710° - 1800°K.)$$

Discussion.—The heat and entropy of the $\beta \rightarrow \alpha'$ transformation are, respectively, 440 cal./mole and 0.45 cal./deg. mole. Corresponding values for the $\alpha' \rightarrow \alpha$ transformation are 3,390 cal./mole and 1.98 cal./deg. mole. It is not possible from the present work alone to derive heat and entropy values for the $\gamma \rightarrow \alpha'$ transformation, but such values are obtainable indirectly. This transformation was shown by the present work to occur near 1120°K., in agreement with the findings of Trömel and Möller.[2] Low temperature heat capacity data of King[8] fix the transformation entropy as 1.67 cal./deg. mole at 298.15°K. This value, in conjunction with entropy increments from Table II, yields 3.07 cal./deg. mole as the transformation entropy at 1120°K. The corresponding heat of transformation is 3,440 cal./mole. The entropies of these transformations appear to be qualitatively in line with the magnitudes of the structural changes.

(8) E. G. King, unpublished measurements of this Laboratory.

THE FORMATION OF OXIDE FILMS AND COPPER POWDER ON THE (111) FACE OF A COPPER SINGLE CRYSTAL DURING THE CATALYTIC REACTION OF HYDROGEN AND OXYGEN

BY ROBERT E. CUNNINGHAM AND F. W. YOUNG, JR.

Contribution of the Cobb Chemical Laboratory of the University of Virginia, Charlottesville, Va.

The catalytic reaction of hydrogen and oxygen was studied on the (111) face of a single crystal of copper in the temperature range of 325 to 425° with oxygen concentrations of 0 to 17 mole %. The surface was examined with elliptically polarized light during the reaction to detect the presence of any oxide films on the surface. Below an oxygen concentration of about 5% no oxide was found, but above 5% films of oxide up to 75 Å. thick were detected. The rates of the catalytic reaction on the (111) face also were measured. When no oxide was present on the surface, the rate was independent of oxygen concentration, but when oxide was present the rate increased with oxygen concentration. Also, when oxide was present, dendritic growths of copper powder formed at polishing imperfections on the surface over a period of several hours. This powder formation resulted in a considerable increase in reaction rate because of the increased surface area. Under conditions of reaction in which no oxide was present the powder slowly disappeared and apparently rejoined the single crystal lattice. As the powder disappeared the reaction rate decreased to its value before powder formation. The powder could not be removed by heating in hydrogen alone, even at 500°.

Introduction

Previous experiments in this Laboratory on the catalytic reaction of hydrogen and oxygen on a copper single crystal have shown the striking rearrangement of the surface to form facets.[1-5] When

the oxygen concentration was greater than about 5%, dendritic growths of copper powder up to sev-

(1) A. T. Gwathmey and A. F. Benton, J. Chem. Phys., 8, 569 (1940).

(2) H. Leidheiser, Jr., and A. T. Gwathmey, J. Am. Chem. Soc., 70, 1200 (1948).

(3) J. B. Wagner, Jr., and A. T. Gwathmey, ibid., 76, 390 (1954).

(4) R. E. Cunningham and A. T. Gwathmey, ibid., 76, 391 (1954).

(5) A. T. Gwathmey and R. E. Cunningham, J. chim. phys., 51, 497 (1954).