drazine should be about 19. From 90–100% hydrazine a much more rapid rise in H_- is anticipated corresponding to the rapid increase in *p*H from 0–5% hydrazine.

There have been several estimates of pK values for weak acids. The most extensive were based on acid–base equilibria in ether.[12] The pK values measured in hydrazine reach, but do not overlap, those measured in ether.

By spectral measurements in dilute aqueous alkali,[13] the pK of *p*-nitrobenzyl cyanide was measured to be 13.4. This is in agreement with the value in Table II (13.43). It is of interest to compare the values of pK derived from spectral measurements in ethanol solution with those measured in aqueous hydrazine: 4-nitrodiphenylamine, pK 20.6 (ref. 8) compared with 15.43 (Table II); trinitrotriphenylmethane, pK 17.44 (ref. 13 and 14) with 14.7 (Table II).

Although 4,4′-dinitrodiphenylmethane (VI) and 4,4′,4″-trinitrotriphenylmethane (VII) were not used as indicators, approximate pK values were determined. With VI it was not certain that the indicator was completely ionized in 66% hydrazine, the highest concentration employed. With VII the color was fleeting so that only approximate measurements could be made. Both VI and VII gave about the same rate of change of H_- with hydrazine concentration as indicators I–V, and are assumed to ionize according to equation (3).

Of the indicators employed, only VI and VII showed a measurable time lag before complete development of color (about 4 minutes with VI and 30 seconds with VII). This agrees with previous observations that the rate of removal of the proton from carbon, in contrast to oxygen and nitrogen, is frequently measurably slow.[14,15] Visually both VI and VII change from colorless in dilute hydrazine to deep blue in 66% hydrazine. In contrast *p*-nitrotoluene fails to show any detectable color in 66% hydrazine.

Bis- and tris-(2,4-dinitrophenyl)-methane gave momentary blue colors at certain hydrazine concentrations, but the colors changed in a matter of seconds to an orange. The orange colored compound failed to act as an indicator in the region studied.

The pK of 1-nitrocarbazole was too high to measure, but it was determined to be greater than 16. Thus a large difference in acidity exists between 1- and 3-nitrocarbazole.

Several diphenylamines and carbazoles containing 2,4-dinitro substitutents were unsatisfactory because the colors were unstable. N-(4′-Nitrophenylazo)-4-nitroaniline was arbitrarily discarded because the data gave a different rate of change of H_- than did the other indicators.

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RECEIVED NOVEMBER 15, 1951

[12] J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[13] R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947).

[14] G. N. Lewis and G. T. Seaborg, *ibid.*, **61**, 1894 (1939).

[15] R. G. Pearson, *ibid.*, **70**, 204 (1948); R. G. Pearson and J. M. Mills, *ibid.*, **72**, 1692 (1950).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Quartz and Cristobalite

BY G. L. HUMPHREY AND E. G. KING

A combination of combustion and solution calorimetry was used to obtain the heats of formation of low-quartz and low-cristobalite from the elements. The results are $\Delta H_{298.16} = -210{,}260 \pm 270$ and $\Delta H_{298.16} = -209{,}330 \pm 250$ cal./mole.

In connection with work on some thermodynamic properties of silicon carbide, we had cause to determine the heats of formation of low-quartz and low-cristobalite. The values obtained differ from those in the literature and also are more precise. A combination of combustion and solution calorimetry was employed in determining the heat of formation of low-cristobalite. Heat of solution measurements served to obtain the heat of transformation of low-cristobalite to low-quartz.

Materials.—The crystalline silicon for the combustion calorimetry was 99.81% pure, according to the manufacturer. The major metallic impurities were determined by spectrographic analysis[1] to be (in %): Mg, 0.007; Al, 0.03; Cu, 0.0025; Ca, 0.02; Cr, 0.005; Ni, 0.002; Ti, 0.0005; and Fe, 0.007. The silicon was ground to −325 mesh with a boron carbide mortar and pestle, and stored in a desiccator containing Dehydrite.

The sample of low-cristobalite, used in the heat of solution measurements, was prepared in this Laboratory[2] from pure quartz (99.9% SiO_2), by prolonged heating at 1480 to 1500°. The X-ray diffraction pattern showed only lines of low-cristobalite, there being no evidence of any untransformed quartz.

Measurements.—The heat of combustion of silicon was determined in apparatus described[3] previously. The energy equivalent of the calorimeter was obtained as 32,384.8 cal./ohm with an average deviation of ±0.02% by combustion of National Bureau of Standards benzoic acid, Standard Sample 39 g. As it was necessary to carry out the calorimetric combustions of silicon under conditions somewhat different than those for the calibration experiments, the energy equivalent was corrected accordingly for each combustion. These corrections averaged 0.06%.

The combustions of silicon were made in silica-glass crucibles that were heavily lined with pure rutile and strongly ignited. (Quartz and cristobalite linings were tried, but their use was precluded by the glassy character of the combustion products.) The oxygen pressure for combustion was 40 atm., and no water was added to the bomb. Samples were ignited by a filter paper fuse without the aid of any kindler. The average size of silicon sample was 0.368 g. mass *in vacuo*. Combustions of the silicon were on the average about 99.9% complete, as determined by strong ignition to constant weight in air of the combustion products. Corrections were applied to the individual heat of combustion

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[1] We are indebted to G. M. Gordon, Division of Mineral Technology, University of California, for this analysis.

[2] We are indebted to R. E. Lorenson for the preparation and testing of this material.

[3] G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).

values for incomplete combustion, and for electrical ignition energy, fuse material, and nitric acid formation in the bomb. The corrections for incomplete combustion ranged from 0.00 to 0.14%. The other correction items totaled from 0.7 to 1.0%.

The silica formed by combustion fell into two categories. The major portion (*ca.* 87%) remained in the combustion crucible along with the rutile liner. X-Ray diffraction of this material showed it to be low-cristobalite. No allowance was made in the calorimetric measurements for possible mutual solid solubility of titania and silica.

The remaining 13% of the silica appeared as a white, very finely divided deposit on the walls of the bomb. This material gave no X-ray diffraction pattern, and strong ignition in air produced no change in weight. Correction for the difference in energy content between this silica and low-cristobalite was made by means of heat of solution measurements.

The solution calorimetry was conducted in apparatus described[4,5] previously. The heats of solution of the finely divided silica from the walls of the bomb and of −325 mesh low-cristobalite were determined in 20.1% hydrofluoric acid at 73.7°. Measurements of quartz had been made[5] previously, under like conditions. The samples were contained in gelatin capsules for dropping into the calorimeter. Corrections for the capsules were made by separate measurements of the heat of solution of gelatin.

Results

All values are in terms of the defined calorie (1 calorie = 4.1840 absolute joules). All weighings were reduced to vacuum, and the molecular weights are in accord with the 1949 International Atomic Weights. The precision uncertainties have been calculated as recommended by Rossini and Deming.[6]

Five determinations of the heat of combustion of crystalline silicon gave 7420.23, 7418.75, 7420.16, 7422.75 and 7421.57 cal./g. The mean value is 7420.69 cal./g., with an average deviation from the mean of ± 0.02%. Corrections for impurities amount to 0.141%, altering the value to 7431.15 cal./g., or 208,520 cal./mole, as the heat of combustion of silicon at 30° under bomb conditions. The corrections to unit fugacity of oxygen, to a constant pressure process, and to 25° lead to the value 209,180 cal./mole, which still must be corrected for the deviation of the solid combustion product from low-cristobalite.

Three measurements of the heat of solution of the fine silica from the bomb walls, in 20.1% hydrofluoric acid at 73.7°, gave −35,410, −35,440 and −35,390 cal./mole for the process

$$SiO_2(25°) + 6HF(sol., 73.7°) = H_2SiF_6(sol., 73.7°) + 2H_2O(sol., 73.7°)$$

The mean, −35,410 ± 30 cal./mole, when compared with the corresponding value for low-cristobalite given below, shows that the fine silica has 1,190 ± 50 cal./mole higher heat content.

Six determinations of the heat of solution of low-cristobalite in 20.1% hydrofluoric acid at 73.7° gave −34,260, −34,200, −34,170, −34,220, −34,240 and −34,240 cal./mole for the process designated above. The mean is −34,220 ± 30 cal./mole. Previous measurements of low-quartz,[5] under identical conditions, gave −33,290 ± 80 cal./mole. Therefore, the heat of transformation of low-cristobalite to low-quartz is $\Delta H_{298.16} = -930 \pm 90$ cal./mole.

Returning to the combustion results, the correction for deviation in heat content of the fine silica deposited on the bomb walls is calculated as 0.13 × 1,190 or 155 cal. This makes $\Delta H_{298.16} = -209{,}330 \pm 250$ cal./mole for the heat of formation of low-cristobalite from the elements. The corresponding heat of formation of low-quartz is $\Delta H_{298.16} = -209{,}330 - 930 = -210{,}260 \pm 270$ cal./mole.

Several values for the heat of formation of quartz have been published by Roth and coworkers.[7] Their results range from −204,000 to −208,300 cal./mole, decreasing chronologically. The value given for cristobalite[7c] is −206,600. It is only recently that crystalline silicon of high purity has been available, which may account for the deviation of these results from those of the present work.

BERKELEY 4, CALIFORNIA RECEIVED NOVEMBER 15, 1951

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(4) D. R. Torgeson and Th. G. Sahama, *ibid.*, **70**, 2156 (1948).

(5) E. G. King, *ibid.*, **73**, 656 (1951).

(6) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(7) (a) W. A. Roth and D. Müller, *Z. physik. Chem.*, **144A**, 255 (1929); (b) W. A. Roth and G. Becker, *ibid.*, **159**, 1 (1932); (c) W. A. Roth and H. Troitzsch, *Z. anorg. Chem.*, **260**, 337 (1949).