ments, and of Henry M. Davis and Dr. George Glockler in the adjustment of the Steinheil spectrograph.

Summary

1. Both allene and methylacetylene are polymerized to white solids when they are exposed (separately) to ultraviolet light.
2. The results of Mooney and Ludlam on the photolysis of ethylene have been confirmed.
3. Qualitative determinations of the long wave length limit of absorption for allene, methylacetylene and vinylacetylene have been made.
4. The quantum yield for the polymerization of allene is 2.5; for methylacetylene, 3.5. For both reactions the quantum yield is independent of the pressure and of the intensity of the absorbed light.
5. A comparison of quantum yields to ion pair yields has been made for four polymerization reactions.

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 17, 1932
PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

Extra Specific Heat in Cuprous Sulfide; Specific Heat of Ferrous Oxide

BY WALTER P. WHITE

Determinations of the specific heat of cuprous sulfide up to 900° have shown a region of abnormally high specific heat at 300° and above, where there is no corresponding crystallographic change of state. Since such variations in specific heat are of recent discovery and are now being studied in various substances, it seems desirable to publish the data. Along with them are given two specific heats of ferrous oxide, determined, apparently, for the first time.

Method and Apparatus

The method is the "dropping" method, with a water calorimeter. The furnace was practically the same as reported on in 1921,[1] platinum wound on a thin-walled alundum tube of 28 mm. inner diameter, and 30 cm. high. At that time there were vertical gradients of 30° in 12 cm. at 900° and a difference of 8° between the specimen and the thermocouple junction immediately beside it. In the present case similar differences were reduced to 2°.

The chief agent in this improvement was a separately heated plug in the furnace bottom, which was disconnected just before being dropped out to make way for the specimen. Since the maximum temperature was only 900° this plug could be more easily made and preserved than in some previous work, where 1400° was reached. A description of this plug will be published elsewhere.

---

[1] Latent heats of melting of nickel and monel metal, White, *Chem. Met. Eng.*, **25**, 17 (1921).

Tests made on another furnace, where a heavy silver tube gave great uniformity of *wall* temperature, had given strong indication that irregularity of temperature was produced in the furnace cavity by conduction of cold down the mullite insulating and supporting tubes. Hence the specimen was supported from below on a small shelf, and was inside a heavy sheet gold cylinder (0.4 mm. thick) closed entirely at the top save for a small hole to admit the platinum thermocouple and its two slender insulating capillary tubes. A Marquardt tube 6 mm. in diameter passing down outside the cylinder acted as a shaft to hold the shelf, and turn it aside in making the drop.

Although the high conducting power of the gold undoubtedly helped to equalize temperature, conduction alone can easily be shown to be of limited value for structures of any size. But the high reflecting power of the surface must have equalized the radiation within the cylinder, and thus diminished the difference of temperature between the specimen and the thermocouple beside it.

A special difficulty arose through the necessity of protecting the specimens from the air. The only trustworthy way to do this appeared at the time to be by inclusion in silica glass tubes. Since these had to be drawn down and sealed after the specimens were in them they had to be rather small, and were actually 1.3 cm. in diameter. As a result the total heat capacity of cuprous sulfide and container averaged over 2.5 times as much as that of the specimen alone, and the accidental error of each final result was therefore around 2.5 times that of the determination which gave it. The ratio for FeO was only a little more favorable.

The heat loss in dropping the specimen, and also much of the systematic error of the temperature distribution in the container, was canceled by the method of the best experimenters, namely, dropping a blank container. The container results at 400 and 700° were obtained by interpolation on a curve derived from the other four results and also from the curve for silica glass published in 1919.

The comparison, summarized in Table I, shows a very significant difference between the older and the newer values. The increase in the mean specific heat of silica glass from the interval 0–300° to the interval 0–900° appears to be 0.0008, or 0.35%, greater by the later determinations, although the heat loss in dropping, which affects the later but not the earlier results, must have lowered the values for higher temperatures more than those for lower. This discrepancy calls for investigation as soon as a suitable furnace is ready. It cannot be due to greater radiation from the furnace to the calorimeter at 900°, for successful and consistent special measurements showed that such radiation caused less than 0.0001° rise. Until this discrepancy is explained we cannot tell whether it makes the low-temperature results for cuprous sulfide too high or too low. If it is due to a difference in the two kinds of silica used, as seems quite possible, of course it causes no error at all. But in any case the resulting error would be only one-sixth of the abnormal difference between the cuprous sulfide specific heats for the two lower intervals, hence it does not shake the evidence for the existence of a real abnormality.

The error from vaporization and splashing as the specimen strikes the water in the calorimeter was completely eliminated by a combination of two excellent devices each of which had previously been used alone by others. These were Plato's narrow cup, knocked under the surface of the water by the specimen falling into it, and a spring shutter, closing the calorimeter top.

In 1920, with temperatures of 1270° and above, each of the "silky" silica inclosures, with one exception, cracked the first time it was dropped into the water. The crack was heard about a minute after the drop, and hence was presumably due to cristobalite formation, which would be effective when the cristobalite inversion temperature, about 180°, was reached in cooling. In the present case all three inclosures, of clear silica, are still intact, though slightly opaque on the surface. That for the cuprous sulfide, after 18 drops, has lost 27 mg. out of 8.18 g. The other two have lost no perceptible weight.

In order to prevent the specimens, which were in small lumps, from packing and splitting the inclosures, they were put in cases of thin sheet metal, copper for the cuprous sulfide, and platinum for the ferrous oxide.

Materials

The cuprous sulfide was a sample of natural mineral which had been analyzed for some previous work.[2] The analysis gave: Cu, 78.68; S, 20.32; Fe, as pyrite, 0.69; SiO_2, none; total 99.78; ratio of Cu to S, 2.032:1. When heated in the unsealed silica tube in a hydrogen atmosphere it lost 22 mg. in about 8.5 g. It is probable that a little of the loss was moisture, but most was sulfur, from the pyrite impurity. The correction for remaining impurities is probably a little under 2 per mille, and negative. On the other hand, the excess copper in the Cu_2S increases the mean atomic weight of it 0.00207 times. If we assume that the mean atomic heat is the same for this mixture as for the pure compound, an assumption surely good to 20% of the small difference involved, the specific heat of the actual mixture is below that of the pure compound by 2 per mille, which almost exactly offsets the other correction, so that the specific heat of the total mass dropped may be taken to be, well within the experimental error, the same as that of the pure material.

The ferrous oxide was some of the material made at the Fixed Nitrogen Research Laboratory for R. W. G. Wyckoff's work on its x-ray structure. The only impurity is magnetite. Dr. H. E. Merwin kindly selected superior lumps by use of an electromagnet, and analyzed them under the microscope. The impurity is about 6%. An approximate correction for this single impurity is given below.

Below 570° FeO is unstable. In order to avoid the effects of the slow transformation which takes place at temperatures somewhat below that, the specimen was put into the hot furnace, rising above 600° in about six minutes.

(2) The sulfides of copper, Posnjak, Allen and Merwin, *Econ. Geol.*, **10**, 508 (1915).

TABLE I

BLANK INCLOSURE OF SILICA, WEIGHT 8.164 G.

Serial number of experiment	23	25	19	21[a]	9	10	8	15
Furnace temp., U°	299.8	299.9	500.3		601.2	601.2	900.7	900.1
Final temp., L°	29.7	29.9	29.9		30.2	30.0	29.5	30.1
Total calories	475.70	475.04	893.14		1115.4	1117.4	1804.7	1802.5
Cal. per gram	58.268	58.188	109.40		136.62	136.87	221.06	220.79
Cal. 0°-L° (calcd.)	5.125	5.160	5.16		5.21	5.18	5.09	5.19
Cal. 0°-U°	63.393	63.348	114.56		141.83	142.05	226.15	225.98
Interval heat	0.21145	0.21123	0.22898		0.23591	0.23628	0.25108	0.25106
Interval heat of silica glass 1919	0.21245		0.23025		0.23666		0.2512	

[a] This determination had a slight mishap. Result omitted.

TABLE III

ABRIDGED, CUPROUS SULFIDE, 30–300°, 400°, 500°, 600°, 900°

Serial number	6	7	24	17	26	16	22	1	2	5	20	3	4
Furnace temp.	300.5	300.4	299.9	399.7	400.3	501.2	500.4	[a]	600.4	601.1	599.4	900.1	899.4
Lower temp.	29.4	29.8	29.8	29.7	29.9	29.5	29.6		29.9	30.1	29.6	30.3	30.2
Total cal.	871.9	869.0	865.1	1256.1	1258.2	1610.2	1606.0		1964.2	1963.4	1955.3	3047.4	3044.0
Total per g. Cu_2S, even intervals	43.66	43.49	43.36	58.35	58.56	71.61	71.69		84.75	84.73	84.39	122.4	122.2
Mean	43.60			58.46		71.64			84.62			122.3	

[a] Result omitted; 11 calories low, or 5.7 per mille. Cause not apparent.

TABLE II

CUPROUS SULFIDE, 30–700°, 8.533 G. Cu_2S

Serial number of experiment	18	27	28
Furnace temp., U°	700.7	700.8	700.9
Final temp., L°	29.9	29.8	29.7
Total calories	2316.1	2317.0	2316.1
Cals., less Cu	2224.9	2225.8	2224.8
Interval heat of silica, 0°–U°	0.24184	0.24184	0.24184
Total heat of silica per g., 0°–U° (calcd.)	169.70	169.76	169.82
Total heat of silica, 0°–L° (calcd.)	5.16	5.14	5.12
Total heat of silica, L°–U°	164.54	164.62	164.70
Total cal. SiO_2	1399.6	1398.8	1399.0
Total cal. Cu_2S	825.3	827.0	825.8
Cal. per g. Cu_2S, L°–U°	96.69	96.89	96.75
Cal. per g. Cu_2S, 30–700°	96.586	96.760	96.594
Average		96.647	

TABLE IV

FERROUS OXIDE, 30–700°. 900°; 10.1058 G. FeO

Serial number	11	12	13	14
Furnace temp.	700.3	700.8	900.7	900.1
Lower temp.	29.8	29.5	29.3	29.5
Total cal.	2779.5	2783.2	3706.8	3704.1
Total per g. FeO even intervals	123.91	123.92	163.22	163.31

The silica glass containers weighed, respectively, 9.1494 g., 8.530 g. and 8.1640 g.

TABLE V

VALUES OF THE HEAT REQUIRED TO RAISE CUPROUS SULFIDE THROUGH SUCCESSIVE INTERVALS

	Calories per gram
300–400°	14.96
400–500°	13.19
500–600°	12.98
600–700°	12.02
700–900°	2 × 12.82

Discussion

A consideration of the discrepancies between the individual observations indicates that the decrease from the second to the third value appearing here may not be real, though it probably is, but that the other changes, and especially that from the first to the second value, do actually exist.

Since only two values for FeO were obtained, the most elaborate equation that can be derived for its specific heat is one of two constants.

Taking such an approximation as the only one available, we have the interval specific heat as

$$0.17508 + 0.0000135t$$

and the true specific heat, therefore

$$0.17508 + 0.000027t$$

This equation is evidently most nearly accurate between 700 and 900°. According to it the interval specific heat increases about 1.44% in 200° near those temperatures. Another oxide of a heavy metal which has been determined with considerable accuracy in this region is zinc oxide.[3] Its interval heat increases a little over 2%, from 0.14370 to 0.14661, in the same interval. The equation for it, holding from 700 to 1100°, is approximately $0.13304 + 0.0000158t - 0.0000000008t^2$, which may give some sort of idea of the deviation from linearity to be expected in such specific heats. The mean atomic heat of the zinc oxide at 800° is 6.35, that of the ferrous oxide, 7.1. The well-known atomic heat curves of oxides are of such a character that the higher the atomic heat is, the less rapidly it increases with temperature.[4] Hence the association of the lower mean atomic heat of the zinc oxide with a higher rate of increase of the heat is entirely normal. This relation, however, properly applies when the atomic heat is below the Dulong and Petit value, 5.96. Its appearance, therefore, when the atomic heat is far above that value is of considerable interest. But it can hardly be discussed adequately without more data.

If we assume that the mean atomic heat of magnetite is the same as that of ferrous oxide the specific heat of magnetite is to that of ferrous oxide as 36:33.14, or, nearly enough, as 12:11. Hence the specific heat of the 6% of magnetite impurity is in the ratio of 6 × 12 against 94 × 11 for the ferrous oxide, and the actual total heat is in the ratio of 72 + 1034, or 1106, against 1100 for pure ferrous oxide. Hence 6/1106 or 0.54% may properly be subtracted from all ferrous oxide values given thus far.

Precision, that is, Agreement, of the Results.—Of the twelve different points determined, one-third show a discrepancy corresponding to 0.8° or over of furnace temperature, or 0.003° of calorimeter temperature, and these discrepancies are about as great at low as at high temperatures. At 700° and above the proportional precision is 1 per mille or better, which is about as good as any previous work, even where conditions were much easier. It agrees rather well with the observed inhomogeneities of furnace temperature. The equally large, and proportionally larger, errors at the lower temperatures are puzzling. Some of the causes of error, including those apparently the most serious, such as furnace temperature heterogeneity, must have been much smaller. The few errors which might have had the same size throughout, such as that in finding the final calorimeter temperature, which was about the same in all cases, are shown by systematic tests[5] and careful study to have been almost certainly negligible.

Lag in the distribution of the furnace temperature, which appeared very strikingly indeed in the studies made on the furnace, and which is greater at lower temperatures, appears, partly by a process of exclusion, to be the

---

(3) Day and White, THIS JOURNAL, **48**, 369 (1926).

(4) Compare White, *Am. J. Sci.*, **47**, 22 (1919).

(5) Particularly the kind described in *ibid.*, **47**, 7, 53, 54 (1919).

only thing which can reasonably be suggested as a cause of these errors. If that is the chief cause, a repetition made with that point in view should increase the precision somewhat. This, however, would be an unprofitable proceeding; a furnace of different type can be made far more precise at lower temperatures than any practicable furnace of wire and refractories can possibly be. Indeed, all other lower temperature specific heat work in our laboratory has been done with a special furnace;[6] and there was no expectation, when the present work was started, of making observations below 600°. These were undertaken when the first results, at higher temperatures, showed that there was something very peculiar lower down. If further examination of the anomaly in Cu_2S near 300° seems desirable, it should undoubtedly be done with a lower-temperature furnace. Meanwhile the data of chief metallurgical importance, at higher temperatures, for which the work was undertaken, seem quite satisfactory, though the proposed reëxamination of the specific heat of silica glass may change them slightly.

Acknowledgment.—Grateful acknowledgment is made to the Phelps Dodge Corporation and to the Carnegie Steel Company, who suggested this work, and contributed liberally to its cost.

Summary

The specific heats of ferrous oxide for the intervals 30–700° and 30–900°, and those of cuprous sulfide for six intervals up to 900°, were determined by the dropping method with various improvements in furnace and calorimeter.

The necessity of inclosing against the air (in silica glass) diminished precision, especially by increasing the amount of dead material and by compelling the thermoelectric thermometer to be outside the sample tested. This about offset the effect of the improvements in apparatus, so that the precision at the higher temperatures only averages the same as in the best previous work.

At the lower temperatures some of the results are not as good.

Over an interval of several hundred degrees, centering somewhere near 300°, there is an excess specific heat in cuprous sulfide of 3 or more calories per gram, similar to those discovered in rhodium near 1300°, in manganese dioxide near 90°K., and in (to date) about a dozen other substances.

WASHINGTON, D. C.

RECEIVED OCTOBER 27, 1932
PUBLISHED MARCH 7, 1933

---

[6] White, *Phys. Rev.*, **31**, 681 (1910).