Fig. 3.—Differential cooling curves.

that the effect of water is reversible. A final experiment was conducted in which twice as much water was added, Fig. 3d. The temperature halt then was observed nearly 50° lower than for the degassed samples. The monohydrate of $FeBr_2$ is not stable at these temperatures (decomposition pressure of H_2O estimated to be 10 atm. at 280°).[2] Previous experiments in this temperature range also have shown no interaction of water vapor with $FeBr_2$ of such a nature to cause a pressure change detectable on a diaphragm gauge.[2]

The marked effect of small amounts of water vapor on the transition temperature again suggests the transition is of the coöperative type. Small amounts of impurities have been shown to have a pronounced effect on second-order type transitions in certain metal systems.[8-10] Water vapor appears to interact with the $FeBr_2$ lattice reversibly in some way which markedly affects the transition. Slightly varying amounts of water vapor could be responsible for some of the differences observed in

(8) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 294.

(9) J. Morin, Phys. Rev., **78**, 819 (1950).

(10) V. Marian, Ann. Phys., **7**, 459 (1937).

the estimated energies of transition and temperatures of the maxima in the heat capacity measurements.

It is of interest to note that the heat capacities of the RP and HCP forms are identical within the limits of our experimental error (rather large, $\pm 1-2\%$) below the transition temperature. Nothing is observed in this temperature range that can be associated with the conversion of one form to the other; presumably both change to the HTF at the transition temperature. From the X-ray data on quenched samples it appears possible to change the RP form to the HCP structure by prolonged heating; this transition occurs more readily at temperatures in the vicinity of 300° when small amounts of water vapor are in the system, which may be related to the observation that the transition to the HTF also then occurs at a lower temperature; the HTF may provide the mechanism for the conversion by reverting to the HCP form on cooling. The transition from RP to HCP appears quite slow in samples thoroughly degassed prior to annealing, surprisingly so even at 500° where 2 hr. annealing was apparently insufficient. This observation may actually be a matter of lack of detection of ordered lines on the powder pattern because of the small particle size of the original dehydrated (RP) sample. A longer annealing interval allows larger crystallites to grow by vaporization.

The calorimeter is currently being redesigned to permit measurement of heat capacities at higher temperature to give better definition of the transition. It is also planned to investigate other substances having similar structural characteristics to those of iron(II) bromide to see whether they undergo similar transitions.

X-Ray Diffraction Pattern for Monoclinic Sulfur

By A. G. Pinkus, J. S. Kim, J. L. McAtee, Jr.,[1] and C. B. Concilio[1]

The X-ray diffraction pattern of monoclinic sulfur has been determined by making use of a special heated sample holder.

In connection with some X-ray diffraction studies[2] on orthorhombic and carbon disulfide-insoluble sulfur, we were surprised to find that an X-ray diffraction pattern for monoclinic sulfur had not been reported.[3] It is noteworthy that although the crystal structure of orthorhombic

(1) Baroid Division, Houston, Texas.

(2) A. G. Pinkus, J. S. Kim, J. L. McAtee, Jr., and C. B. Concilio, This Journal, **79**, 4566 (1957).

(3) After our work was complete (J. S. Kim, thesis, Baylor University, 1957) a notice of a preliminary report of the diffraction pattern of monoclinic sulfur came to our attention [C. A., **51**, 10965 (1957)] The abstract of the paper presented at a meeting of the American Physical Society, Southeastern Section at the University of Florida, Gainesville, Florida [J. E. Miller, N. S. Kendrick, Jr., and G. W. Crawford, Phys. Rev., **99**, 163 (1955)], however, does not present any data for comparison with our results.

though the crystal structure of orthorhombic sulfur is well-established,[4,5] only a preliminary report on the unit cell and space group of monoclinic sulfur has been published using single crystal data.[6] The reasonable assumption has been made[4] that monoclinic sulfur consists of a cyclic ring of eight sulfur atoms. Das[7] recently enumerated the difficulties encountered in his unsuccessful attempts to obtain a powder X-ray pattern of monoclinic

(4) B. E. Warren and J. T. Burwell, J. Chem. Phys., **3**, 6 (1935).

(5) S. C. Abrahams, Acta Cryst., **8**, 661 (1955).

(6) J. T. Burwell, II, Z. Krist., **97**, 123 (1937).

(7) S. R. Das in "I U P A C Colloquium Münster, on Silicon-Sulphur-Phosphates," Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse 1955, p. 103.

TABLE I

X-RAY DIFFRACTION DATA ON MONOCLINIC SULFUR

d_{obsd}	(I_1)	Q_{obsd}	Q_{calcd}					h,k,l
6.65	26	0.0226	0.0232					111
6.32	4	.0250						
4.41	5	.0514						
3.79	13	.0696						
3.74	20	.0714	0.0718,	0.0712				221, 122
3.29	100	.0924	.0928					222
3.10	9	.1040	(.1056)					(213?)
3.04	12	.1082	.1083					032
3.00	4	.1111	.1110					123
2.60	2	.1479	.1481					141
2.49	7	.1613	.1622,	.1601				412, 214
2.46	6	.1652	.1666					042
2.44	4	.1679	.1673,	.1673,	0.1675			323, 240, 124
2.18	3	.2104	.2100,	.2109				340, 143
2.10	2	.2267	.2267,	.2267				234, 502
1.932	1	.2678	.2678,	.2672,	.2678			144, 343, 252
1.894	2	.2787						
1.872	3	.2853	.2850					350
1.857	6	.2900	.2890					325
1.786	3	.3135	.3131,	.3144,	.3137			434, 601, 415
1.708	2	.3427	.3422,	.3419,	.3419,	0.3421,	0.3424, 0.3416	353, 261, 054, 045, 154, 306
1.679	1	.3546	.3562					245
1.635	5	.3741	.3749,	.3750				326, 063
1.599	2	.3910	.3917,	.3915				543, 632
1.567	3	.4072	.4080					070
1.452	17	.4743	.4748					346
1.432	3	.4876	.4875					463

sulfur. He obtained only lines characteristic of orthorhombic sulfur and postulated that the transition from monoclinic to orthorhombic must have occurred during the process of powdering and/or the time of exposure to X-radiation. In another experiment only the orthorhombic pattern was obtained for sulfur particles imbedded in celluloid film at temperatures from 80 to 114°.

In the present work, using a recent device for heating the sample holder,[8] a sample of purified orthorhombic sulfur was heated and the diffraction pattern determined immediately on solidification. The data are shown in Table I. Calculated and observed Q values along with the corresponding hkl indices are also in Table I. The Q-values were calculated on the basis of the cell constants reported by Burwell.[6]

Four of the observed d-lines do not correspond to calculated Q values. On the basis of further experiments, it seems reasonable that the 3.79 line in the monoclinic pattern represents the appearance of the 3.85 line of orthorhombic sulfur, this being the strongest line in the orthorhombic pattern. Since the calculated and observed Q-values for the 3.10 line do not check closely, it is possible that a similar explanation may hold here, this line possibly representing the 3.11 or one of the neighboring lines of the orthorhombic pattern. It is evident from a comparison with the orthorhombic diffraction pattern in Table II that the remaining three lines at 6.32, 4.41 and 1.894 cannot be explained similarly. A reasonable explanation of these lines is that they stem from some substance intermediate in the transformation from monoclinic to orthorhombic sulfur. It may be that this

is the γ-(or "nacreous")-sulfur first discovered by Muthmann[9] and more recently investigated by Briske and Hartshorne[10] in their studies on transformations of γ-sulfur to orthorhombic and monoclinic sulfur. Evidence that the extra lines are not due to impurities in the sulfur are (1) the use of highly purified sulfur, (2) the fact that the *same* sample after standing for 24 hr. gave a diffraction pattern with no extraneous lines being present. The diffraction data for this sample after standing for 24 hr. are listed in Table II. Thus, although the diffraction pattern of the 24-hr. sample shows only 19 lines, all of these lines correspond[11] to 19 of the 45 lines in the orthorhombic pattern. The lesser number of lines in the 24 hr. sample is due to the difference in the methods of obtaining the diffraction patterns. Thus, for the orthorhombic sulfur, a rotating sample holder[12] was used. This makes possible the obtaining of a more nearly complete and accurate diffraction pattern since it minimizes orientational effects in powdered samples. Orientational effects, however, might be expected to be present for the monoclinic patterns since the sample is in the form of a thin film. This would tend to decrease the number of observed lines. Furthermore, an exact matching of intensities would

(8) R. A. Roland and E. J. Weiss, *Am. Mineralogist*, **41**, 117 (1956).

(9) W. Muthmann, *Z. Krist.*, **17**, 336 (1890).

(10) C. Briske and N. H. Hartshorne, *Disc. Faraday Soc.*, **23**, 196 (1957).

(11) One of the referees has pointed out that the d-values for the material after 24 hr. are consistently larger than the corresponding data for pure orthorhombic sulfur and that a definite pattern seems to emerge since Δd varies regularly from 0.05 at the lowest scattering angle to 0.002–0.003 at the highest scattering angle. Thus, this would appear to be the result of systematic error in measurement rather than orientation. We thank the referee for pointing this out.

(12) J. L. McAtee, Jr., *Am. Mineralogist*, **41**, 942 (1956).

TABLE II

X-RAY DIFFRACTION DATA ON SULFUR SAMPLES

Monoclinic after 24 hr. d	(I/I₁)	Pure orthorhombic² d	(I/I₁)	Monoclinic after 24 hr. d	(I/I₁)	Pure orthorhombic² d	(I/I₁)
		7.62	6			1.959	5
		5.75	10	1.906	25	1.901	8
		4.17	1	1.829	6	1.823	8
4.11	14	4.06	16			1.783	3
3.90	100	3.85	100	1.760	7	1.757	7
		3.56	7	1.726	12	1.725	13
3.48	37	3.45	19			1.696	6
3.36	38	3.34	31			1.668	1
3.24	76	3.22	39	1.649	8	1.649	3
3.14	59	3.11	21			1.622	8
		3.09	15	1.607	12	1.604	5
		2.85	15			1.561	2
		2.68	3			1.535	3
2.63	8	2.62	11	1.531	8	1.529	2
		2.57	5			1.499	1
		2.50	9			1.474	3
2.43	54	2.43	10			1.457	2
2.39	10	2.38	9			1.437	4
		2.29	4			1.418	4
2.15	8	2.14	3			1.388	2
2.13	16	2.11	14			1.351	3
1.996	35	1.988	3			1.305	2
						1.279	2

of plastic sulfur to the rhombic form[14] and more recently it has been reported that rhombohedral sulfur (S_6) is converted to a mixture of plastic and orthorhombic sulfur on exposure to X-rays.[15]

In some further experiments in which crystallization of the melted sample was induced by various methods (touching with a spatula, tapping the side of the holder, etc.) various anomalous patterns were obtained which could not be indexed as completely, using the monoclinic cell constants. We have not yet been able to assess completely the significance of these results. Whenever the sample was allowed to crystallize undisturbed, however, reproducible patterns were obtained.

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Experimental

Sulfur was purified by the method used in the previous paper.[2] Diffraction patterns were obtained on a North American Philips X-ray diffractometer using Cu Kα radiation. In the tables, d is the interplanar spacing in Å. calculated from the Bragg law: $d = \lambda/2 \sin \theta$ where λ is the wave length of radiation used = 1.540 Å. and θ is the angle of diffraction. (I/I_1) is the relative intensity in % based on the most intense line taken as 100 where I_1 is the strongest line and I is the intensity of the respective line.

Values for Q_{obsd} were obtained from the relationship[16a]: $Q_{obsd} = 1/d.^2$ The following relationship for monoclinic crystals (second setting) was used to compute Q_{obsd} values[16b]

$$Q_{calcd} = (1/d_{hkl})^2 = \frac{h^2}{a^2\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta}$$

where $a = 10.90$, $b = 10.96$, $c = 11.02$ and $\beta = 83°16'$ as given by Burwell.[6]

not be expected for the two samples for the same reason.

In view of the recent experiments of Hartshorne and co-workers on the rate of transformation of monoclinic to rhombic sulfur,[13] it would appear certain that the conversion to orthorhombic sulfur should be complete in 24 hr. It would seem possible that the rate of this conversion may be increased by the X-ray irradiation. It has been shown that this is the case for the transformation

(13) N. H. Hartshorne and M. Thackray, J. Chem. Soc., 2122 (1957), and earlier papers.

(14) H. Müller and E. Schmid, Monatsh. Chem., 85, 719 (1954).
(15) J. Donohue, A. Caron and E. Goldish, Nature, 182, 518 (1958).
(16) D. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958. (a) p. 274, (b) p. 49.

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Voltammetry with Linearly Varying Potential: Case of Irreversible Waves at Spherical Electrodes

BY RICHARD D. DeMARS[1] AND IRVING SHAIN

The theory of voltammetry with linearly varying potential has been extended to the case of irreversible electrode reactions at spherical electrodes. Theoretical current–voltage curves were constructed from the results of a numerical calculation which assumed a first-order electrode reaction occurring at potentials where the rate of the back reaction is negligible. The curves make it possible to determine the kinetic parameters of the electrode reaction from an experimental irreversible wave. Effect of variation of any of the experimental parameters was also considered. The theory was checked by comparison with current–voltage curves obtained for the reduction of iodate ion.

In the course of recent work on the analytical applications of the hanging mercury drop electrode using the techniques of voltammetry with linearly varying potential,[2–4] irreversible reactions were encountered which could not be interpreted by the theory for diffusion currents at spherical

electrodes developed by Frankenthal and Shain[5] and by Reinmuth.[6] These irreversible waves are characterized by peaks which are lower and which span an unusually wide range of potentials. Both of these effects are drawbacks from an analytical point of view. The fact that these kinetic effects can be observed, however, indicates that the method may be of use in the investigation of slow electrode processes.

(1) Based in part on the Ph.D. thesis of Richard D. DeMars, University of Wisconsin, 1958. General Electric Fellow, 1957–1958.
(2) J. W. Ross, R. D. DeMars and I. Shain, Anal. Chem., 28, 1768 (1956).
(3) R. D. DeMars and I. Shain, ibid., 29, 1825 (1957).
(4) K. J. Martin and I. Shain, ibid., 30, 1808 (1958).

(5) R. P. Frankenthal and I. Shain, THIS JOURNAL, 78, 2969 (1956).
(6) W. H. Reinmuth, ibid., 79, 6358 (1957).