adsorbed molecule can be held jointly by two walls or that there are impurities in the surface that increase the attraction of some sites for adsorbate. As noted above, the new Graphon has a small portion of super-active surface amounting to some 3% of the total. The old Graphon apparently had about 50% of the surface more active than the average, since the heat curves dropped until the surface was about half covered.

When a surface is heterogeneous the writers feel that the computation of spreading pressures from isotherms may be misleading. Adsorption will tend to be localized on a non-uniform surface, the first molecules migrating to the sites of highest activity and remaining there. Only when all surface sites are of equal activity will an adsorbed film behave as a true two dimensional gas and spread uniformly.

ADDED IN PROOF.—A recent paper by Halsey,[14] not available when this manuscript was submitted, contains several points of interest in relation to the present results. We agree with Halsey's conclusions regarding the importance of coöperative forces in adsorption but feel that his equations do not adequately describe real isotherms. In Fig. 2 of his paper Halsey shows the calculated isotherm for a uniform surface to rise more steeply than the one for a surface of "great heterogeneity." Our experimental results show just the opposite effect; the Spheron isotherm is much steeper initially than the Graphon isotherm. Halsey assumes that the isotherm for a very inhomogeneous surface may have a pseudo "point B" far below completion of the first layer. This again is contrary to what we find for Spheron and to the majority of isotherms in the literature. In his calculated isotherm for the uniform surface, where coöperative adsorption is important, Halsey gives a curve concave to the pressure axis below point B, contrary to the actual behavior of the Graphon isotherm. We find no indication in the ethyl chloride isotherm of stepwise adsorption as postulated by Halsey, but as noted above[13] isotherms of others at liquid nitrogen temperature have shown such a behavior.

Another reference not previously noted is the work of Jura and Criddle,[15] who find the isotherm of argon on a graphite sample to have the convex shape below point B that we find for the Graphon isotherm. This provides still additional indication that the true isotherm for a uniform surface must have this shape.

[14] G. D. Halsey, "The Role of Surface Heterogeneity in Adsorption," Volume IV, Advances in Catalysis, Academic Press, Inc., New York, N. Y., 1952.

[15] G. Jura and D. Criddle, *J. Phys. Colloid Chem.*, **55**, 163 (1951).

CLAREMONT, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

Purple Sulfur, A New Allotropic Form[1]

BY FRANCIS OWEN RICE AND CALVIN SPARROW

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According to vapor pressure measurements, sulfur vapor in the pressure range 0.1–1.0 mm. and the temperature range 500–700° consists almost entirely of S_2 molecules. We have found that these may be frozen out on a liquid nitrogen cooled surface to give a purple solid. On warming to room temperature, this changes in the course of a few seconds, to a mixture containing about 40% of crystalline sulfur and 60% of amorphous sulfur. The activation energy of the change is 3.1 kcal.

A very large number of allotropic forms of sulfur has been reported and detailed confirmation of the existence of at least three forms has been published. At ordinary temperatures the stable solid form consists of an S_8 ring.[2] At temperatures above about 160°, liquid sulfur consists largely of long chains which on sudden cooling to room temperature form the unstable amorphous sulfur, $S\mu$. In the temperature range 500–700° and the pressure range 0.1 to 1.0 mm., the vapor consists essentially of S_2 molecules formed by dissociation of S_8 in accordance with the equilibrium,[3] $S_8 \rightleftarrows 4\ S_2$. Both solid and liquid sulfur are diamagnetic but the vapor is paramagnetic[4] and measurements on the susceptibility of sulfur vapor indicate that S_2 has the theoretical moment of the triplet state. There is some uncertainty as to the method of dissociation of sulfur in the vapor state and intermediates such as S_4 and S_6 have been postulated in order to reconcile vapor pressure and vapor density measurements. In the following series of equilibria

$$S_8 \rightleftarrows 4S_2 \qquad S_6 \rightleftarrows 3S_2$$

$$S_4 \rightleftarrows 2S_2 \qquad S_2 \rightleftarrows 2S$$

it seems to be fairly well established that at 450° the vapor consists of over 99% S_2 at 0.1 mm. pressure, and 55% S_2 at 1 mm. pressure. At 500°, the vapor consists of almost 100% S_2 at either 0.1 mm. or 1.0 mm. pressure. The dissociation of S_2 into monatomic sulfur begins to be appreciable only at very high temperatures (1200°) even at 0.1 mm. pressure.

The present investigation was undertaken with the object of studying these equilibria by attempting to isolate one of the high temperature forms, S_2, using a technique described in a previous article[5] in which an equilibrium or stationary state was established at high temperatures in a flowing system at low pressures and the gases were suddenly cooled

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[1] Taken from the dissertation presented by Calvin Sparrow for the Degree of Doctor of Philosophy in The Catholic University of America.

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

[3] G. Preuner and W. Schupp, *Z. physik. Chem.*, **68**, 129, (1909); W. Klemm and H. Kilian, *ibid.*, **B49**, 279 (1941); H. Braune, S. Peter and V. Neveling, *Z. Naturforsch.*, **6a**, 32 (1951).

[4] L. Néel, *Compt. rend.*, **194**, 2035 (1932); A. B. Scott, THIS JOURNAL, **71**, 3145 (1949).

[5] F. O. Rice and M. Freamo, *ibid.*, **73**, 5529 (1951).

to the temperature of liquid nitrogen. In this way one can "freeze" an equilibrium and study the products at leisure.

The preliminary work was done in the temperature and pressure range in which, according to vapor density measurements, the vapor consists of over 95% S_2 molecules. We have found that if sulfur vapor at about 500° and at a pressure of 0.1 to 1.0 mm. be suddenly brought in contact with a liquid nitrogen cooled surface, the sulfur condenses as a purple solid. This solid is stable indefinitely at liquid nitrogen temperatures but when warmed to room temperature, changes to yellow sulfur in the course of a few seconds. At $-80°$, the change from purple to yellow is quite noticeable after a few hours.

Some years ago Staudinger and Kreis[6] predicted that S_2 would be a deep blue gas (b.p. $-30°$) which would readily polymerize to S_8 or S_x. They tried unsuccessfully to prepare S_2 by means of a "hot–cold" quartz tube, one end of which was immersed in liquid air and the other end, containing a small quantity of sulfur, was heated. We have repeated their experiments and have confirmed their conclusion that "in the hot–cold quartz tube under vacuum and cooled by liquid air we were only able to condense amorphous sulfur, not a trace of blue sulfur." The failure is due to the sulfur not reaching the cold part of the tube but condensing on the walls at ambient or somewhat lower temperatures. If this source of error is avoided by having a liquid-nitrogen cooled finger just beyond the furnace and pumping continuously so as to keep the pressure at the cold finger below about 10^{-3} mm. the S_2 may be readily condensed to give a purple solid.

Purple sulfur prepared in this way can be scraped off the cold finger under liquid nitrogen as gray-black chips. It has a negligibly small vapor pressure and cannot be sublimed at any temperature at which it is stable. It is insoluble at $-80°$ in propane, dimethyl ether and toluene and at their normal boiling points, in ethylene and ethane. There is a slight solubility in carbon disulfide at $-80°$, probably due to small amounts of S_8. Purple sulfur is a non-conductor of electricity, does not fluoresce in ultraviolet light and does not emit visible light when changing to yellow sulfur. Since we did not have the facilities for measuring magnetic susceptibilities at low temperatures, measurements on purple sulfur are being conducted at other laboratories. We hope that comparison of the results of measurements made by the method of paramagnetic resonance, with the results obtained by other methods involving the weight of the sample, will enable one to estimate unequivocally the percentage of S_2 present in purple sulfur. We have not been able to devise any other method of analysis for purple sulfur or the blue material,[5] $(NH)_x$.

When purple sulfur is warmed to room temperature, the resulting yellow sulfur is quite rubbery. We therefore made a series of determinations in which we conducted the transformation of purple to yellow sulfur at various temperatures and extracted any crystalline sulfur by refluxing with carbon disulfide. The results (Table I) show that the yellow sulfur resulting from purple sulfur contains approximately 40% of crystalline sulfur and 60% of amorphous sulfur and these proportions are independent of the temperature of conversion.

We then measured the rate of change of purple to yellow sulfur at various temperatures by taking advantage of the change in color. White light was passed through a yellow filter, focused on the sample and the intensity of the reflected light measured by a photoelectric cell and galvanometer.

TABLE I

PER CENT. BY WEIGHT OF SULFUR INSOLUBLE IN CS_2 IN PRODUCT RESULTING FROM THE TRANSFORMATION OF THE PURPLE FORM TO YELLOW

Temp. of transformation, °C.	Percentage of insoluble sulfur				Mean
0	60.5	55.3	62.8	61.9	60.1
25	59.1	55.8	66.0	64.6	61.4
100	57.2	56.6	69.0	50.1	58.2

The rate of change, measured in arbitrary units of galvanometer deflections, showed an initial rapid reaction for the first minute or two followed by a slower change occurring at constant speed. Apparently the change starts at the surface and goes into the solid. We were not able to measure the initial rapid reaction due to difficulties in obtaining the zero point and obtained the activation energy of 3.1 kcal. from the slope of the curve obtained by plotting the inverse of the absolute temperature against the logarithm of the speed after the initial rapid reaction. This is shown in Fig. 1.

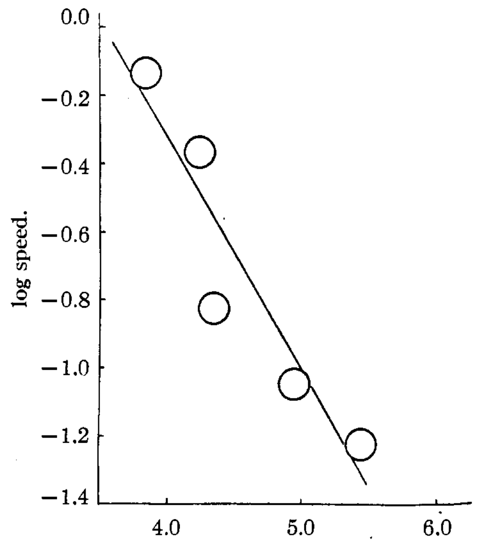

Fig. 1.

It seems likely that purple sulfur consists of loosely coupled S_2 molecules since the purple form is obtained only by freezing sulfur vapor when it consists, according to vapor density measurements, predominantly of S_2 molecules. The hypothesis that purple sulfur is S_2 is further supported by the fact that in the vapor state[7] the S_2 molecule shows

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(6) H. Staudinger and W. Kreis, *Helvetica Chimica Acta*, **8**, 71 (1925).

(7) G. Herzberg, "Spectra of Diatomic Molecules," Second Edition, 1950, D. Van Nostrand Co., New York N. Y., p. 566.

some absorption in the region 8125–6940 Å. which is consistent with condensation to a purple solid. We did many experiments at different pressures, both at very high temperatures (up to about 1250°) and at low temperatures (down to about 120°) but did not succeed in obtaining evidence of any other form of sulfur except S_2 and the ordinary yellow form, S_8.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY AT BROWN UNIVERSITY]

An X-Ray Study of Potassium Laurate Solutions[1]

BY DONALD E. ANDERSEN[2] AND GENE B. CARPENTER

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The small-angle X-ray scattering from concentrated solutions of potassium laurate has been reinvestigated with the use of monochromatic radiation. A correction for the effect of the slit height has been applied. The measured intensity has been used to calculate the radial distribution function for the potassium gegenions which sheathe the laurate micelles. Ambiguities in the interpretation have been reduced by theoretical arguments and by comparison of the distributions calculated on the basis of alternative assumptions. For 30% (by weight) solutions, the micelle centers form a loose close-packed arrangement; the arrangement becomes less ordered as the concentration is decreased. The effective micelle diameter is 27 Å. and the average micelle contains about 63 molecules. Detailed conclusions regarding the structure of the micelles cannot be obtained from the data reported.

Introduction

Numerous studies[3] have attempted by means of X-ray diffraction to obtain information about the structure of the micellar aggregates which are believed to exist in soap solutions. Differences in the interpretation of the results have, however, persisted, and serious objections to most of the published work have recently been emphasized.[4] First, several of the models proposed[5,6] for micelles have been based on distances calculated from the positions of diffraction maxima under the assumption that Bragg's law remains meaningful for the scattering from non-periodic structures. Second, previous workers have assumed that the use of filtered characteristic X-radiation gives scattering patterns negligibly different from those which would be produced by strictly monochromatic radiation. It may be added, third, that when slits rather than pinholes were used to define the incident beam, it has been previously assumed that no correction was necessary.

The present investigation has aimed at avoiding these sources of uncertainty by use of a crystal monochromator, by correcting for the effect of slit height and by calculating a radial distribution function from the observed data.

Experimental

A Norelco Diffraction Unit, operated at 35 kv. and 20 ma. with a copper-target tube, was used for the production of X-rays. A nearly monochromatic beam was isolated by reflection from the (001) face of a pentaerythritol crystal. The small-angle vacuum camera was similar to that described by Kiessig[7] except that the collimating system consisted of a pair of lead-jawed slits 10 cm. apart instead of a pair of pinholes. The distance from sample to film was 22.4 cm.; this was determined by photographing a sample of powdered lauric acid, which has a known shortest spacing of 27.4 Å. The cell for solution samples was a small brass box with mica windows spaced 0.170 cm. apart. Solutions were introduced into the cell by means of a hypodermic syringe.

Solutions of potassium laurate were freshly prepared before each exposure by neutralizing weighed amounts of lauric acid with standard potassium hydroxide solution and then adjusting the amount of water to give the desired concentrations. Lauric acid was obtained from the Paragon Testing Laboratories. It was vacuum distilled and recrystallized from absolute ethanol. The purified material melted between 43.6 and 44.3°.

Four concentrations of potassium laurate were investigated: 29.6, 24.1, 19.7 and 15.1% by weight. The exposure times were 48, 70, 95 and 135 hours, respectively, so that investigations at lower concentrations become increasingly difficult. After each exposure a calibration photograph was prepared by making a set of timed exposures of the direct beam filtered through aluminum to obtain a convenient intensity. Corresponding diffraction and calibration photographs were developed simultaneously with Kodak D-11 developer.

Film densities were measured with a Sinclair Smith recording microphotometer, which, however, was operated manually to obtain maximum reproducibility. Figure 1 represents typical microphotometer tracings. For each concentration several photographs were prepared and microphotometered, and the resulting diffraction curves were averaged. The fluctuations in the individual microphotometer tracings can only be attributed to the grain of the film.

Since, for X-rays, exposure time is proportional to intensity,[8] it was possible to convert these traces to a (relative) energy scale by use of the calibration films. The curves of Fig. 2 which are drawn through the experimental points present the relative diffraction intensities for each concentration as functions of diffraction angles. Since the pentaerythritol monochromator crystal deteriorated in the X-ray beam, the calibration prepared at the end of an exposure of a certain solution does not allow the intensities to be placed on an absolute scale. Thus the intensities from the various concentrations are only approximately comparable. The experimental intensity values, I_e, are related to the absolute intensity values, I_a, by the equation $I_a = cI_e + k$ where c and k are unknown constants, differing from one solution to the next.

Corrections for absorption in the sample and for polarization of the incident beam by the monochromator were nearly constant over the range of angles studied; hence these corrections were neglected.

The Slit Height Correction.—Small angle diffraction is often observed with a beam defined by slits, rather than by pinholes, in order to decrease the long exposure times.

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[1] Based upon a thesis submitted by D. E. Andersen to Brown University in partial fulfillment of the requirements for the Ph.D. degree.

[2] du Pont Predoctoral Fellow, 1950–1951.

[3] W. Philippoff, *J. Colloid Sci.*, **5**, 169 (1950) (this review contains a comprehensive bibliography); G. W. Brady, *J. Chem. Phys.*, **19**, 1547 (1951).

[4] E. W. Hughes, *Nature*, **166**, 1017 (1950).

[5] W. Philippoff, *Kolloid-Z.*, **96**, 255 (1941).

[6] W. D. Harkins, *J. Chem. Phys.*, **16**, 156 (1948).

[7] H. Kiessig, *Kolloid-Z.*, **98**, 213 (1942).

[8] K. Lonsdale, "Crystals and X-Rays," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 35.