Si–Si–R_3 or R_3Si–O–SiR_3, from the corresponding silicon halides, leads to complete fission of the Si–Si or Si–O–Si bonds (resulting in the formation of tetrasubstituted monosilanes), it has been found that by interrupting the synthesis so as to execute it in two stages, this fission may be largely eliminated.

2. In this way $(C_6H_5)_6Si_2$, $(C_6H_5)_6Si_2O$ and $C_6H_5SiCl_3$, hitherto obtainable from Si_2Cl_6, Si_2OBr_6 and $SiCl_4$, respectively, only by means of the Grignard reaction, have been prepared.

3. Hexabenzyldisilane, m. p. 194°, has been synthesized from Si_2Cl_6 and benzylsodium, as well as by the Grignard reaction between Si_2Cl_6 and benzylmagnesium chloride.

CAMBRIDGE, MASS. RECEIVED OCTOBER 23, 1940

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, STATE COLLEGE OF WASHINGTON]

Compressed Films at Solid–Liquid Interfaces[1]

BY J. L. CULBERTSON AND L. L. WINTER

Recent studies of the densities of silica gel and active ash-free charcoal as measured by means of various liquids acting as buoying fluids clearly supported the concept that when a solid is wetted by a liquid a definite compression of the liquid occurs in the interfacial layer.[1a] If such be the case, it is obvious that the compressed layer must suffer changes in its properties commensurate with the degree of compression, and such changes have been observed in connection with many other studies. For example, the freezing point,[2] vapor pressure[3] and dielectric constant[4] of adsorbed liquids have been investigated with indications of decided property changes. While the effect has been described as a compression, it is extremely unlikely that the molecular attraction which is the causal factor may be considered as strictly analogous to a physical pressure. This must be true in all cases in which the liquid molecules possess any degree of dissymmetry, for in such cases tendencies toward molecular orientation would be a natural consequence.

Numerous studies,[5] both with organic and inorganic material, have been made of the extent of liquid binding at solid–liquid interfaces. Considering only those in which aqueous systems have been investigated, most have been concerned with a determination of "bound" water, and the methods used may be classified as calorimetric, cryoscopic, and dilatometric. No critical comparison of these methods will be attempted in this paper, but it is pointed out that in view of the fact that the properties of the "bound" liquid are undoubtedly quite different from the normal ones, it is obviously impossible for any such method to yield absolute values of the quantities of the affected substance, if, in the application of the method, calculations are made that are based on the normal physical constants of the liquid. In view of this fact no emphasis is laid in this paper on the absolute quantities of water affected by the forces at the solid surface, but the writers consider that the comparisons made of the same interface under different conditions and of the different interfaces are valid and significant.

Since previous studies of the heat of wetting[6] indicated marked variations in the intensity of binding of liquid at various solid surfaces, it was decided to make a comparison of the silica–water and the carbon–water systems by this method.

Materials, Apparatus, and Method.—The silica gel and active ash-free carbon were identical with those previously used and their preparation has been described.[1a] The experimental method consisted in determining the amount of water which, at equilibrium, remained unfrozen in a sample of a known weight of the solid in the presence of an excess of water. These determinations were made at various temperatures below the normal freezing point of the water. The apparatus consisted of a freezing-bath for freezing the sample and a calorimeter in which the ice was melted. The freezing-bath was made from a low 1.2-gal. Dewar vessel which was closed with a two-inch Celotex cover. In the cover were mounted, (a) a cali-

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[1] Original manuscript received November 20, 1939.

[1a] Culbertson and Dunbar, THIS JOURNAL, **59**, 306 (1937); Culbertson and Weber, *ibid.*, **60**, 2695 (1938). *Cf.* also Harkins and Ewing, *ibid.*, **43**, 1787 (1921); Lamb and Coolidge, *ibid.*, **42**, 1146 (1920); Marinesco, *Compt. rend. soc. biol.*, **103**, 872 (1930); Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930); Stamm and Hanson, *J. Phys. Chem.*, **41**, 1007 (1937).

[2] St. John, THIS JOURNAL, **53**, 4014 (1931).

[3] Lambert and Foster, *Proc. Roy. Soc.* (London), **A134**, 246 (1931).

[4] Marinesco, *Compt. rend. soc. biol.*, **103**, 872 (1930); *J. chim. phys.*, **28**, 51 (1931).

[5] Jones and Gortner, *J. Phys. Chem.*, **36**, 387 (1932); Foote and Saxton, THIS JOURNAL, **39**, 627 and 1103 (1917).

[6] Culbertson and Winter, *ibid.*, **59**, 308 (1937).

brated low temperature thermometer, (b) a brass tube, closed at the lower end, which extended almost to the bottom of the vessel and served as a well into which the sample container was lowered, and (c) a motor driven stirrer. The calorimeter, a 1000-ml., cylindrical, Dewar flask closed with a thick cork stopper, was mounted in a water thermostat maintained at 25° (±0.1°). In the calorimeter stopper were mounted calibrated Beckmann thermometers, a heating element, and a motor-driven stirrer. The sample container consisted of a cylindrical stainless steel vessel closed by a water-tight screw plug of the same material. It was machined from a (plus) one inch solid rod and measured 1 × 4.25 in. outside dimensions, 0.875 × 3.75 in. inside dimensions. Inside the container were fitted four radial stainless steel webs extending from the outside wall two-thirds of the way to the center. These were electrically welded to the walls and were designed to increase the heat conductivity from container to sample.

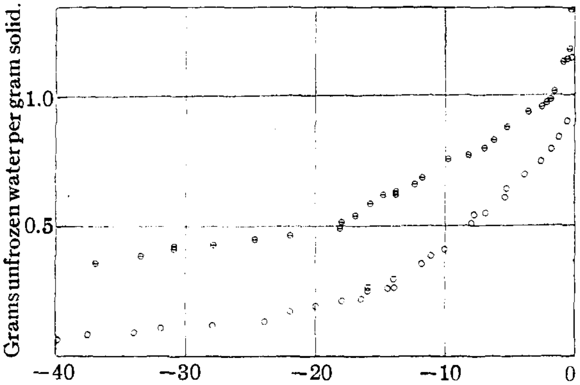

Fig. 1.—Unfrozen water per unit weight of solid *versus* temperature: ⊖, silica gel–water; O, carbon–water.

Determinations were made as follows. A sample of about 5 g. of the solid was weighed accurately into the steel container and a weighed quantity of water (12 g. or more) added to it. The container was then placed in a closed vessel connected to a vacuum pump and the space evacuated to a pressure of approximately 25 mm. in order to remove air from the surface of the solid and permit complete wetting. Wet filter paper in the evacuated space during this step was provided in order to decrease evaporation of water in the container and blank determinations made with and without the evacuating step checked very closely, indicating that the moisture loss during evacuation was very small. After evacuation, the sample container was closed and lowered into the brass tube in the freezing-bath, where it was allowed to remain for from four to eight hours in order to attain a constant temperature. In order to obtain constant temperature freezing conditions, salt–ice mixtures were used for temperatures between 0 and −20°. For temperatures below −20° solid carbon dioxide–ether mixtures were used, and constancy of temperature was maintained by dropping in small pieces of solid carbon dioxide in the manner described by Dunn.[7] Just before transfer of the frozen sample from the freezing-bath to the calorimeter, the heat capacity of the entire assembly of the latter was determined by means of the electrical heating unit in the usual manner. The transfer of the sample container from the freezing-bath to the calorimeter was effected with the greatest possible dispatch. The container was attached by means of a silk thread to a cork which fitted the openings in both the brass tube of the freezing-bath and the closure of the calorimeter. Only this cork was touched in making the transfer, and a considerable study was made of this phase of the manipulation until assurance was gained that errors were reduced to a minimum.

In order to calculate the unfrozen water present in the system a modified form of St. John's[2] equation was used.

Results and Discussion

The results of the two series of measurements are shown graphically in Fig. 1. If it may be assumed that the specific areas of the two solids are comparable, then the unfrozen water layer on the silica is greater than on the charcoal. This undoubtedly indicates a greater binding force for the water at the silica than at the carbon surface, which is in agreement with the previous density[1] and heat of wetting[6] studies. The assumption of equal areas is uncertain, though for somewhat similar systems Bartell and Fu[8] found values of the same order of magnitude. The steeper slope of the carbon curve throughout most of the temperature range also would suggest that the water binding was less effective at the carbon than at the silica surface. In the lower temperature range the curve representing the carbon becomes flatter than that for silica, but only when the quantity of unfrozen water on the carbon becomes very small. In this region the solid–unfrozen water ratio becomes much greater for the carbon than for the silica.

Marinesco[4] has suggested that water strongly adsorbed at the surface of colloidal systems might be present in the form of one of the high pressure crystalline states. If this were the case, at temperatures below the triple point representing the equilibrium between liquid, ice I, and ice III, in the pressure–temperature diagram for water, no unfrozen water should remain in the systems considered here. Unfortunately the lack of data on the specific heats and heats of fusion of the high pressure forms of ice makes it impossible to investigate this suggestion quantitatively in the present study. It appears, however, that should this offer a satisfactory explanation of these systems, then at the temperature of the triple point referred to, about −22°, the curves

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[7] Dunn, *Science*, **69**, 359 (1929).

[8] Bartell and Fu, *Coll. Sym. Annual*, **7** 135 (1929).

plotted from the data should present unique characteristics. This is not obvious in the figure though the curves have attained a linear form from about this temperature to the lowest temperature investigated which was −50°. Clearly we may not describe the water which freezes only at temperatures below −22° in terms of ordinary phase equilibria. That which freezes at temperatures between zero and −22° might be so described if it is considered as compressed but other evidence indicates that orientation of the dipoles would complicate the interpretation. In conclusion it may be stated that the present data are in general agreement with the previous studies[1a,6] and while compression occurs at the solid–liquid interface, the properties of the liquid are additionally modified in this region.

Summary

By means of the calorimetric method, determinations have been made of the unfrozen water on the surface of wetted silica gel and carbon at temperatures from 0 to −50°. Basing a comparison on unit quantities of the solids, the silica binds the water more strongly than the carbon.

PULLMAN, WASHINGTON RECEIVED SEPTEMBER 10, 1940

[CONTRIBUTION FROM THE CHEMICAL SECTION, DRUG DIVISION, AND THE MICROANALYTICAL DIVISION OF THE FOOD AND DRUG ADMINISTRATION, FEDERAL SECURITY AGENCY]

The Dimorphism of Sulfathiazole

BY DONALD C. GROVE AND GEORGE L. KEENAN

The entrance of the new drug, sulfathiazole (2-sulfanilamidothiazole),[1] into the field of chemotherapy made a survey of its physical and chemical properties essential. In the course of this study, it was found that sulfathiazole occurred in two distinct crystalline forms. The conditions for the existence and isolation of these dimorphs and their physical properties are herein presented.

Hexagonal Form.—When sulfathiazole was crystallized from water, acetone, or ethyl or methyl alcohol, hexagonal prisms (Fig. 1) were formed. They were obtained easily by preparing a saturated solution of the material in ethyl alcohol on the steam-bath, removing the container from the bath and allowing to cool slowly to room temperature. The crystals were then filtered off and dried in the air.

On heating the hexagonal prisms on the Fisher micromelting point stage and observing under the microscope, part of them remained clear and melted at approximately 173 to 175°, while others suddenly turned white or opaque throughout and did not melt until the temperature reached 200–202°. This indicated that some of the crystals had undergone a transition to the higher melting form, and the extent of this transition has been found to depend to a large extent upon the rate of heating. Thus, if the stage was preheated to about 175°, it was possible to observe all the crystals melting at this temperature. On the other hand, if the temperature was raised slowly, most of the crystals would have become opaque before reaching 173°.

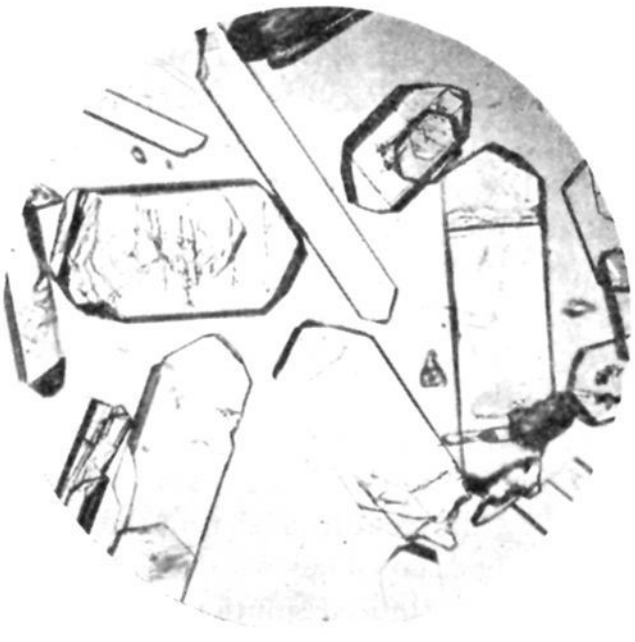

Fig. 1.—Hexagonal prisms (× 80).

Rod Form.—An attempt was made to isolate a second type of crystal by fractional crystallization from hot ethyl alcohol; however, all fractions obtained in this manner were of the hexagonal form. Consideration was then given to the fact that when the hexagonal form became opaque upon heating on the melting point stage, it had in reality undergone a structural change to the higher melting form. This opaque material then, if used as a seed crystal, should give rise to the higher melting form. Accordingly, a hot satu-

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[1] Fosbinder and Walters, THIS JOURNAL, **61**, 2032 (1939).