Calorimetric Method for the Determination of the Surface Energy of a Brittle Crystalline Solid

A. Kenneth Schellinger

School of Mineral Sciences, Stanford University, Stanford, California

Measurement of the surface energy existing at a solid-gas interface has presented experimenters with a difficult problem because of the rigidity of the interface. The surface energy of a gas-liquid interface can be determined with some precision by noting the energy necessary to deform the interface by a known amount. The problem of solid surface energies has received attention from a number of research workers; one of the earliest of these, Gibbs (*3*), defined the surface energy of a solid as that energy necessary to produce a unit of new surface on the solid. The Gibbs-Thomson relationship, an outgrowth of his work and others', can be used in the thermodynamic approximation of solid surface energies. This equation gives a relationship between particle size and vapor pressure for small particles of a solid:

$$RTln\ X_s/X = 2M\gamma/rd$$

where M is the mol wt of a solid, γ is the free surface energy, r is the radius of curvature of the small particle, d is the density of the solid, X_s is the higher vapor pressure of particles of radius r, and X is the normal vapor pressure of large particles of the solid.

Centnerszwer and Krustinsons (*2*) used a modified form of this relationship to calculate the surface tensions of oxide and carbonate metallic salts, such as mercuric oxide and silver carbonate. Measurement of the vapor pressures and particle radii of these solids allowed calculations of surface tensions ranging from 3,000 to over 100,000 dynes per cm. Other workers, in general, found values of a lower order of magnitude for the surface energies, or tensions, of solids. Values obtained experimentally by a number of methods indicate that the order of magnitude of solid surface energies may be between 100 and 1000 ergs/cm^2. Most of these experiments were performed on soluble ionic solids of a rather soft nature, notably halide salts. No universally acceptable experimental method has yet been published, and agreement as to the order of magnitude of these important physical constants has not been achieved among research workers.

The lack of adequate data on the surface energies of minerals has been a handicap felt particularly by workers in the fields of comminution and froth flotation. Estimates of doubtful validity have placed the surface energy of quartz, a common industrial mineral, at about 1,000 ergs/cm^2. Use of this figure in the calculation of the efficiencies of industrial ball mills has yielded remarkably low results, on the order of 1%. Gross and Zimmerly (*4*) used a drop-weight method for crushing quartz and an HF acid dissolution method for estimating the surface produced, and found that some 56,000 ergs of work was necessary to produce a square centimeter of new quartz surface. No heat loss measurements were made during their experiments, which were primarily designed to measure the crushing resistance of various minerals.

When a brittle crystalline solid is comminuted, the particle size is reduced and the surface is increased. Energy is consumed in the actual rupture of ionic and atomic bonds, in the production of slippage on crystal planes, in the production of twins and other atomic rearrangements, and in the production of heat by internal friction below the elastic limit. The energy of slip, twinning, and bond rupture is stored in the system as potential energy and heat energy is liberated from the crystalline system by conduction and radiation. The energy of bond rupture is termed the surface energy and is probably very large as compared with the energy of slip and twinning, particularly in a hard substance such as quartz. Therefore, if the comminution process were carried out inside a calorimeter, the total heat energy liberated by both friction in the comminuting medium and in the crystalline solid could be measured. Furthermore, an accurate determination of the energy input to comminution would permit calculation of the net energy going to the creation of new surface, that is, to the rupturing of atomic bonds. Estimation of the net new surface produced by an increment of energy is possible by the BET (*1*) method of gas adsorption at low temperatures. From this information, calculation of the specific surface energy of the comminuted solid is possible. The method makes no provision for the effect of crystal slip and twinning, or for the adsorption of gases that may be present in the comminuting calorimeter. The energy effect of these should be small.

A calorimeter was constructed to experiment with this proposed method of determining the total surface energy of crystalline solids. This calorimeter consists of a brass chamber 3 in. in diam suspended inside a stainless steel water jacket, so that it can be completely surrounded by water except for two brass suspension bearings affixed to each end. A Beckmann thermometer was inserted into the water bath, and could be read to the nearest hundredth of a degree Centigrade and estimated to one-thousandth of a degree. The brass chamber was filled with about 200 g of the crystalline solid and 3 kg of chilled steel shot. Revolution of the whole assembly on its longitudinal axis, suspended on ball bearings, caused tumbling of the charge mass and comminution of the brittle solid. A calibrated spring and sprocket arrangement was used to turn the calorimeter and gave the net energy input to the tumbling mass with good accuracy. The thermometer revolved with the calorimeter without affecting its calibration. The whole assembly was placed inside a wooden box whose air temperature was controlled at 20°–25° C ± 0.1° C by compressed air, a cooling coil, and a thermoregulator. Heat loss from the calorimeter shell was determined and formed the basis of a heat loss curve so that this factor was always known. The calorimeter constant was derived by use of the heat of solution of NaOH in water. Calibration of the whole assembly was achieved by using only the steel shot in

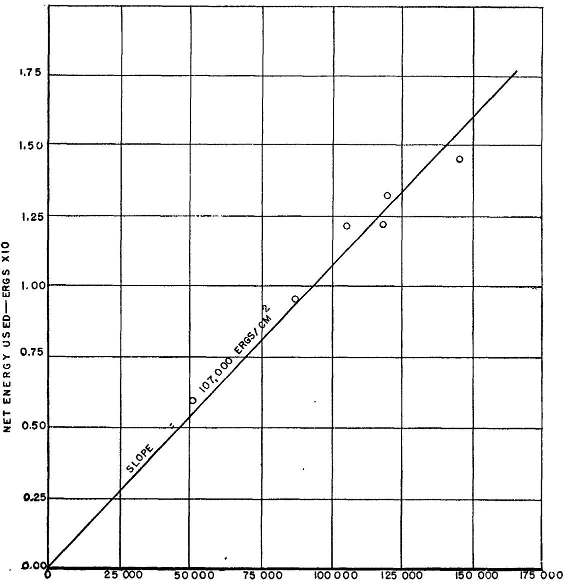

FIG. 1. Surface energy of quartz sand.

the chamber. Under these conditions, the kinetic energy input balanced the energy output as heat when the calorimeter was revolved for a short length of time. No breakage occurred under these conditions, and all of the energy input became heat energy through friction of the tumbling mass. However, when a brittle material such as quartz was added to the chamber and was comminuted, the energy output was about 10%–20% lower than the energy input. By the reasoning already outlined, this difference was considered to remain on the brittle material as surface energy.

The total surface on the brittle solid was measured both before comminution and after comminution by the rather well-known method of BET adsorption isotherms, using CO_2 gas as the adsorbate. The net surface produced during the comminution was thus obtained by subtraction and, divided into the net energy difference, gave the specific surface energy of the brittle crystalline solid.

The calorimeter was used to derive the surface energy of quartz by making a series of determinations on a glass sand made up of quartz grains. The net energy consumption—that is, the energy to create new surface—was plotted against the net surface produced (Fig. 1). A straight line is seen to average the six points determined and, moreover, to pass through the origin of the plot as it should. The slope of this line is considered to give the average total surface energy of the quartz sand. It is 107,000 ergs/cm². The deviations of the individual points from the straight line are not large. The order of magnitude of this surface energy figure for quartz is not seriously in conflict with the figures mentioned earlier in this article, and seems to agree in a qualitative way with the difference in hardness of a substance like quartz and a substance like mercury with a surface energy of approximately 473 ergs/cm² at room temperature.

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Some Derivatives of Diphenyldisulfide with Antispirochetal Activity[1]

P. Pratesi, L. Raffa, B. Babudieri, and A. Nascimbene

Istituto Chimico Farmaceutico, Università, Pavia,
Istituto Superiore di Sanità, Roma, and
Laboratorio Batteriologico della Provincia, Pavia, Italy

Among the few synthetic and natural disulfides (gliotoxin) which have been studied chemotherapeutically, no substances of therapeutic importance have been found. This may be the result of the low activity of these substances or of their unfavorable chemotherapeutic ratio. Research on bis(4-aminophenyl)disulfide makes it seem possible that the disulfides constitute a class of chemotherapeutic agents distinct from the sulfonamide drugs, and active through a different mechanism, which has not yet been defined (*4*).

For some time two of us (P. P. and L. R., *5*) have focused our attention on bis(2-aminophenyl)disulfide and its related compounds. McDonagh (*1, 2*) recognized the activity of bis(2-aminophenyl)disulfide against *Spirochaeta pallida*; we have since found that this substance is also active against *Borrelia recurrentis* (*3, 6*).

In view of the antispirochetal activity of bis(2-aminophenyl)disulfide, we thought it would be interesting to see whether correlations analogous to those existing between *p*-amino-substituted disulfides and sulfonamides in *coccus* infection would hold good also for spirochetal infection in the series of *o*-amino derivatives. For this purpose, a series of *o*-amino sulfamides was prepared, that is: 2-aminobenzenesulfonamide, 2-(2-aminobenzenesulfamido)-pyridine, 2-(2-aminobenzenesulfamido)-4-methylthiazole, and 2-(2-aminobenzenesulfamido)benzenesulfamide, in order to see if these substances would show antispirochetal activity greater than that already observed in bis(2-aminophenyl)disulfide.

Research on the activity of these compounds against *Spirochaeta hispanica* and *Treponema brucei* in mice was performed by Prof. D. Bovet at l'Institut Pasteur, Paris, and has given completely negative results (*6, 7*). This confirms the distinction between the class of disulfides and that of the sulfonamides as chemotherapeutic agents.

Among the derivatives of bis(2-aminophenyl)disulfide previously synthesized by us, one of the most interesting was the *N*-disuccinyl derivative (*3, 6 7*). Although its average lethal dose (13 mg per 20-g mouse) is only a

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