

## Surface Energy Calculations

September 13, 2001

Surface energy is the popular term given to the interfacial tension of a solid. To explain this, first think of a liquid. The tension across a liquid-vapor (liquid-gas) interface is called surface tension and is written  $\gamma_{LV}$ . This is actually well defined. It would seem that you could define a similar term for a solid and write it  $\gamma_{SV}$ . In fact you can *define* it but you cannot *measure* it. The physical reason for this is that a solid will not deform the way a liquid will; more specifically, a solid will support a shear stress.

Young's equation expresses the equilibrium situation:

$$\gamma_{SV} - \gamma_{LS} = \gamma_{LV} \cos \theta$$

where  $\theta$  is the contact angle. The left hand side is what we can calculate from the things we can measure on the right hand side. We can only calculate the *difference* between the two quantities on the left hand side. In essence,  $\gamma_{SV}$  hides behind  $\gamma_{LS}$ , which is the interfacial tension between the liquid and solid. We have one equation and two unknowns.

There is no exact answer to this dilemma. There are models which provide *approximate* answers by giving us another equation with which to separate  $\gamma_{SV}$  and  $\gamma_{LS}$ . It is very important to understand that these are, indeed, very approximate. The models are based on independent knowledge of how liquids and solids adhere to one another. There are five models, which are widely used, and a number of others which have their own small followings. These five models are often called by different names, so it becomes tedious to keep track of all of them. For the record, these models and their synonyms are

1. Zisman critical wetting tension
2. Girifalco, Good, Fowkes, Young combining rule
3. Owens, Wendt geometric mean
4. Wu harmonic mean
5. Lewis acid/base theory

For well-known, well-characterized surfaces, there can be a 25% difference in the answers provided by each model. Each model does better with one type of surface or another, but there is no recognized "correct" answer.

Why do people bother with surface energy? Primarily they would like to characterize surfaces without having to explicitly describe the test fluid. The right hand side of Young's equation is the product of the test liquid surface tension and the contact angle, so surface energy is more "fundamental," even if it cannot be accurately measured with today's understanding. Secondly, the surface energy description mimics the surface tension description for liquids, so similar terminology is used for both. Thirdly, the inaccuracies in today's models are acceptable to some.

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How do you calculate surface energy?

1. Measure contact angles with test fluids for which you know the surface tension.
2. Choose a model to supply the missing equation. See what others in your industry have chosen.
3. Enter the surface tension for the test liquids and the measured contact angles for each in the Surface Energy Calculator. This is purposefully left as a manual transfer because you may wish to average many readings before entering the data. After you choose the model, you click *Contact Angle* → *Surface Energy* and the equations are solved.

In one sense, this is very easy, taking only three steps. However, in another sense, it is subtle because you are restricting the available answers when you choose the model. The real issue is choosing a model.

The models vary significantly in complexity. The biggest difference is how many *different* test liquids are required for a *single* determination. If a model requires two liquids, contact angles must be measured with both liquids on the sample. Obviously, one measures at different, but close, positions on the sample with each liquid. The Girifalco model is the only model that provides an answer with only one test liquid. The Zisman model requires at least two fluids, although using more improves the results. (The Zisman calculator is located separately under Tools.) The geometric and harmonic mean models require two test fluids and the acid/base model requires three. Furthermore, the geometric, harmonic, and acid/base models require additional knowledge about the test fluids (these parameters are provided for common test fluids in the FTA software). All of these models are discussed in basic physical chemistry references, a list of which is provided in the Help file. A real understanding of them requires substantial study.

A good place to start is the Girifalco model with water as the test liquid. This is the simplest and gives a good idea of what the surface energy is. The Girifalco model is best at low contact angles and worst at high. Because the model has an adjustable parameter,  $\Phi$ , which is normally set equal to 1, the model can be tweaked to provide better answers at high contact angles. By “better,” we mean more like the other models. To do this, we must have a “known” surface energy and contact angle. We use Teflon as the reference material and call this the FTA extended Girifalco model.

Finally, most workers use surface energy numbers on a relative basis in the final analysis. For example, if they wish to increase the wettability of a polymer by plasma treatment, they would be happy by a change of 20 to 30 but they would be just as happy with a change of 25 to 35.