



Transparency with Thermodynamics

Thermodynamic models are an aid to predicting the properties of glass and provide an insight into the progress of reactions in the manufacture of glasses and multi-component industrial products.

► How can a glass be manufactured that has exactly the property profile desired or that stands up well to defined loading? As long ago as the 19th century Otto Schott recognized that it was not possible to successfully tackle such a demanding problem purely on a trial and error basis. Rather it was necessary to take a long-drawn-out experimental approach based upon a scientific understanding of the material in its liquid and solid state. Since then noteworthy progress has been made, particularly in the fields of mineralogy, geology, metallurgy and chemical engineering. Efficient and practically oriented working models were developed. Unfortunately glass never quite kept pace with other developments. Glass technologists remained more or less dependent for many decades on the tedious trial-and-error method. The increasing amount of experimental data available improved the situation. Experimental data was collated in extensive databases, linked, statistically evaluated and, when necessary, extrapolated into the unknown territory of unresearched glass compositions. However, this approach can only be looked upon as makeshift. It provides us with no new knowledge and thus does not create a basis for innovation.

Structure or specific heat: the thermodynamic perspective

Traditionally, the preferred way of explaining the properties of glasses and glass melts, and their dependence on their composition, was from the structural angle. This also made sense in light of the enormous success of structural concepts in crystallography and solid-state physics.

Network models and models of the chemical bond of glasses were developed which afforded deep insights into the difference between crystalline and non-crystalline materials. However, the comment by one skeptic that “these concepts explain everything and predict nothing” cannot be dismissed completely. The structural explanation of glass is a one-sided explanation. Glass should be described, like any other material, by using two complementary images: a structural one that describes atoms in specific positions, chemical bonds, etc. and a thermodynamic one that covers such things as temperatures, heat content and chemical reaction energies. For glasses, for which far less detailed knowledge is available about their structures than is the case with crystalline solids, the thermodynamic perspective is particularly important and relevant.

A model for describing glass

Three things are required to draw up a thermodynamic model for glass. Firstly we have to put aside our reservations about the non-equilibrium of the glassy state. Tabulated data for the glassy state – is that possible? Every textbook on glass refers to this fact: The properties of a solid glass depend not only on its composition but also on its past history. That does not mean, however, that the thermodynamic data on glass are “somehow uncertain”. The precision with which the density or the

refractive index, for example, of an industrial product can in fact be set to an accuracy of four or five places proves the opposite. Secondly, we can describe a glass via its energy difference to its crystalline counterpart. The energy (thermodynamic) state of any glass differentiates it from its crystalline counterpart only by a relatively low energy difference, a property known as its glass forming energy. Thirdly, and this is the biggest challenge, we have to develop a strategy for identifying this crystalline counterpart for a given glass composition, not just for some simple model glasses, but also for multi-component industrial products. Today these three means are already available to us in a sufficiently precise form, and they are being continuously refined and improved. As a result, glass technologists can now use the full range of thermodynamic data in the same way that their colleagues in the areas of chemistry and metallurgy have been doing for years.

Desktop design of new glass compositions

It is already possible to reliably model many properties of glass and to draft them on the computer before needing to carry out the first trial melts. We expect that the systematic application and logical extension

of the concept will make it possible for the old time-consuming and cost-intensive trial-and-error method to be largely replaced with the development of glass compositions with the desired new properties. In this case the term "properties" refers not only to various material data such as density and thermal expansion coefficient, but also to complex behavior patterns such as chemical resistance. Using the three-part model, such complex patterns can be opened up with ease. Let us consider, for example, a glass subjected to a corrosive liquid. The problem breaks down into three parts that can be tackled separately:

Glass	→	Crystalline counterpart
Crystalline counterpart	→	Individual oxides
Individual oxides +		
Liquid	→	Reaction products
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Glass + Medium	→	Reaction products

Basis for a quantitative high temperature reactor technology

In the same way the melting of a glass from a recipe of raw materials can be analyzed by tackling the following problems:

Raw materials	→	Individual oxides+ Batch gases
Individual oxides	→	Crystalline counterpart to glass
Crystalline counterpart	→	Glass
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Raw materials	→	Glass + Batch gases

In this way we gain access to the reversible and irreversible energy shares involved in industrial glass melting. As shown for countless industrial batch formulae, the accuracy of today's modeling is better than 5 percent. The application of the model, as just described, does not necessarily lead to innovative glass compositions, but it does form the basis for a quantitative high temperature reactor technology for the glass melt. ◀



Structure State

Ordered / Disordered,
Short-range Order /
Long-range Order

Solid / Liquid
Elastic / Fluid

X-ray Scatter
Colors

Specific Heat
Viscosity

Chemical Bond

Phase Diagram

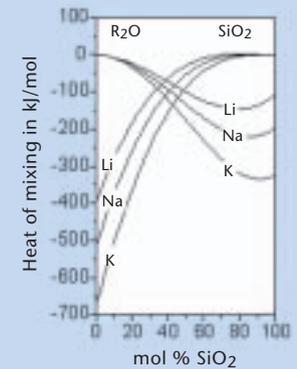
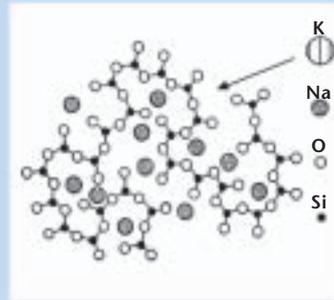
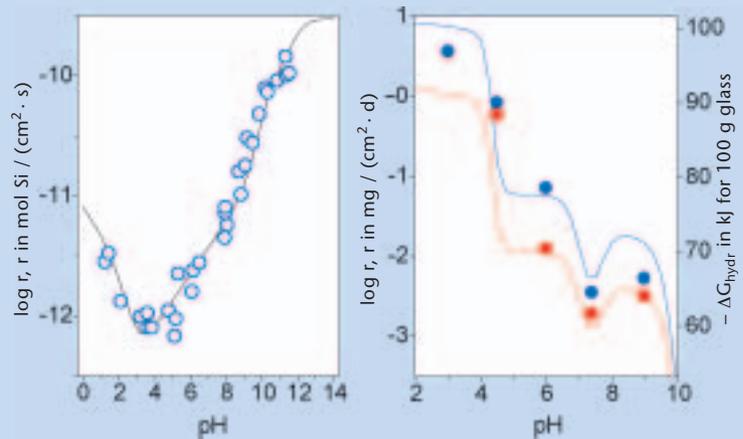


Illustration of the structural and thermodynamic view of glass

The illustration makes this clear with an example. Here Na^+ ions are replaced in a soda-lime silicate glass by large K^+ ions. The illustration of the structure shows that exchanging ions in this way sets up compressive stress in the glass matrix (which is actually the case: the effect is used to chemically toughen glass). Only the thermodynamic illustration shows that the implantation of a K^+ in a silicate glass is more favorable from the energy aspect than that of a Na^+ , even though the K^+ virtually has to squeeze in and in so doing causes mechanical stress



Comparison of modeled and experimentally determined dissolution velocities of glasses. The illustration on the left shows the accuracy of the model for a pH electrode glass subjected to a saline solution. The diagram on the right shows the results of a desktop development with the objective of a completely different pH dependence of the chemical resistance (in fact with a very low resistance in the acid range and a relatively high resistance in the neutral range). Experiments carried out subsequently prove the accuracy of the prediction.