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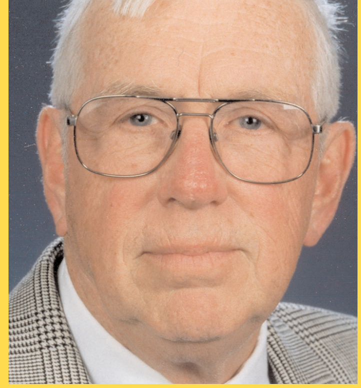
Good ol' thermodynamics



Last September, I participated in the most recent conference in the series *Thermodynamics of Alloys* in Rome. The occurrence of a meeting on this subject in Rome seemed quite appropriate, as I will try to explain.

If you haven't noticed, research in thermodynamics, for the sake of accurately determining experimental data or interpreting existing data, is not a subject riding the crest of current popularity. I would not like to propose a research project of this sort to a funding agency. Nevertheless, thermodynamics is still, or should be, a primary consideration in the conduct of research on nearly any materials-related subject. Thermodynamics has a variety of interesting and useful facets, providing different criteria, limits, and 'predictions' for many different sorts of applications: the limits on the efficiency of heat engines from the Carnot cycle, the inherent increase in entropy (at constant q and V) leading to disorder in the universe, and the decrease in Gibbs energy (constant P and T) for spontaneous reactions, etc. To a student taking a thermodynamics course, the subject seems so 'theoretical' that the important experimental foundations for the subject can get lost in the equations. But for the most practical aspects of the subject (in my opinion, the calculation and interpretation of the Gibbs energy changes associated with potential reactions), the intelligent use of software and databases can save much time and effort wasted on experiments intended to 'see if a reaction will go'.

I like to tell students that thermodynamics is an experimental science, where some expert in a laboratory has measured the necessary parameters much more accurately than he/she could hope to do and that these results have been cataloged for our use, to save us from doing unnecessary experimentation. Of course, some of the most useful thermodynamics results are presented as graphical representations: Ellingham phase stability diagrams, Pourbaix E versus pH diagrams, Kellogg volatilization diagrams, etc., which are also available from software. These programs are indispensable in evaluating multiphase, multicomponent equilibria such as in combustion product gases or CVD processes, or 'Phacomp' analyses of condensed systems (solids and liquids). We, and others, have used thermodynamic modeling to interpret the existence and relative stabilities of the several oxyfluoride solutes in cryolite-base fused salts. The breadth of thermodynamics applications is truly amazing.

At the meeting in Rome, it occurred to me that thermodynamics supports materials research in a similar manner as Latin has provided a useful basis for learning some European languages and, perhaps, as Roman engineering and architecture has led to our modern environment. Although the usage of Latin as a language has died, it must still be considered as a useful discipline in a high school curriculum for learning grammar and developing vocabulary essential to the study of English and other languages. Latin sets up the rules for language development in a manner that thermodynamics forms a basis for proper conduct of materials research, following certain rules and respecting known limitations. Lest my thermodynamics friends become too unhappy with me, I admit that new materials topics do arise where reliable experimental data are lacking, so that the calorimeters, the Knudsen cells, etc., must be dusted off and returned to use. Certainly, many electrochemical systems (batteries, sensors, and fuel cells) enjoy current popularity and importance. There also remains a need to improve or change some very old classic processes, such as the 115-year-old Hall-Heroult process for manufacturing primary aluminum, a sort of 'trailing edge' research opportunity.

The materials research and funding communities increasingly shift their emphasis to chase new topics: now nanotechnology, computer modeling, and biomaterials, following monolithic ceramics, composites, intermetallic compounds, and superconductivity, to name but a few. I hope that the importance of thermodynamics as a useful and necessary tool for any new materials topic is not forgotten. With that realization, thermodynamics courses will be retained in relevant materials curricula, leading to judgement, economy, and efficiency in students' and researchers' future materials experimentation and interpretations.

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