Physical Chemistry and Materials

Teaching of Chemical Thermodynamics using Available Data and an Innovative Approach

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Abstract

Analysis is made showing how Helmholtz and Gibbs energies conveniently interrelate enabling typical 2-D and 3-D curves to be drawn across a range of temperature for selected chemical equilibria. Opposing influences leading to a free energy minimum or an entropy maximum are given a physical explanation with the attainment of equilibrium and the choice of conditions made evident. Simplifying assumptions are emphasised and the examples show how the data are manipulated, limits evaluated and trends in equilibrium summarised by EXCEL charts.

Level of Material: Second Year

The Execution

Chemical thermodynamics seeks to make some sense out of the nature of chemical reactivity and in particular the circumstances that bring change to an individual reaction and govern the condition known as chemical equilibrium. Undoubtedly the progression to a rounded view of equilibrium thermodynamics comes with a fuller appreciation of the mathematics applied. This develops as students seek out relevant data to analyse using appropriate relationships and techniques for evaluating limits, testing maxima and minima and processing with EXCEL or similar.

The approach evolved as students showed a preference for accessing their own data in lecture examples and tutorial problem solving. Lab programmes were adjusted to suit convenient data acquisition using familiar reaction processes such as volatile liquid vaporisation and more time was released for data manipulation and mathematical processing. Generally practical work allows less time for the data analysis and often proceeds with linear plots to determine for instance enthalpies of vaporisation. With a different emphasis the same data can be treated more extensively to produce a family of dipping free energy curves portraying typical equilibrium minima over a range of temperatures. As well as being visually more attractive this analysis gives quantitative information on how equilibrium minima shift with temperature rather than qualitative indications associated with Le Chatelier type predictions based on enthalpy change alone.

Traditionally chemists concern themselves with the Gibbs energy function almost exclusively for describing reaction equilibria and assert that the Helmholtz energy function is less useful in chemistry because processes and reactions are more often carried out at constant pressure than at constant volume. This view however is unnecessarily restrictive and leads to a lack of use of Helmholtz energy to describe chemical systems such as vaporisation and thermal decompositions where a change of perspective from Gibbs energy is particularly informative and appropriate. The method builds on the familiarity with Gibbs energy, its relationships, approximations, conditions and transformations applied in dealing with reactivity of a chemical process and the establishment of dynamic equilibrium. A wealth of thermodynamic data is available and listed for convenient access in summary form particularly at 298 K fixed temperature and 1 bar standard pressure. Thus standard Gibbs energies of reaction are easily calculable at 298 K and at other temperatures with reasonable accuracy by further processing. However to apply these data modifications to depict how Gibbs energy changes during a constant T,p reaction we find that unless mixtures of gases are involved then we cannot illustrate free energy descent to a typical equilibrium minimum (a highly emphasized feature of equilibrium thermodynamics). This restriction may be overcome and so encompass a much wider range of reactions by transforming the data set from Gibbs to Helmholtz energies and considering the consequence to the free energy profile for reactions maintained at constant V,T. Such a shift allows quite an intriguing insight into the circumstances that bring about reactants changing to products then establishing equilibrium at a position intermediate to full conversion. Certainly this gives a powerful demonstration of the enabling mathematics to model such processes and is firmly based on evidence and experience gained rather than allowed to remain as concepts within theoretical discussion.

Pre-requisite Knowledge

By the end of the first year students have encountered the analytical methods required and have reasonable confidence with data analysis packages and of seeking IT/mathematical support. Nevertheless care is taken to reconsider the methods appropriate to the task in hand and this can be usefully combined with introductory discussions to the laboratory/tutorial groups undertaking particular reaction investigations.

How Are Students With Different Mathematical Backgrounds Supported?

Pre-course and remedial classes during the first year contribute together with availability of personal skill development in tutorials, surgeries and general accessibility to maths/IT staff.

What Support Was Needed?

Discussion with other staff helped give shape to the approach gradually adopted. It was decided early on that the data analysis and information portrayal should be conveniently managed by using EXCEL. Technical support with some of the teething problems was provided by IT staff and this extended the analysis to other reaction types as further aspects of study became apparent.

The Barriers, Enablers and Evidence of Success

There is some initial resistance to using Helmholtz energy, a thermodynamic function that is relatively unfamiliar and often taken at face value to be of secondary importance to Gibbs energy in contributing to an understanding of chemical reactivity. This is not helped by the sparse development of the Helmholtz energy function generally given by most undergraduate textbooks. Conversely though this helps bring freshness and an element of research to the application in the lab and problem solving. This becomes apparent when the information aspects obtained from the interrelationship of the two free energy functions can be readily accessed and convincingly portrayed.

How Can Other Academics Reproduce This?

A more detailed description of the methodology is available with examples of reaction types and interpretation of results from free energy profiles showing minima corresponding to dynamic equilibrium positions and related entropy terms producing maxima. This information can be found at the following URL **www.mathcentre.ac.uk/resources/casestudy/burgess_a_casestudy.asp**

Quality Assurance

The lab reports showed a freshness and individual commitment towards the assignments. Thermodynamic questions in examinations requiring data acquisition were more frequently attempted, more detail presented and though inappropriate data could be selected the method of approach to problem solving could be credited and a general improvement in answer standard noted.

Other Recommendations

Availability of an adequate data book in lectures, labs and tutorials on an individual basis was essential and opened up opportunities to show how data might be accessed from different tables and the same data directed to portraying different aspects and modified for other physical conditions.

In dealing with data manipulations with terms arising that show indeterminate values for the EXCEL charts it is a good opportunity to highlight methods of obtaining limiting values (a particular case is for terms similar to $x\ln x$ where x is at or near to zero).

Opportunities exist to consider a variety of reaction types and propose more investigative content for lab/tutorial assignments. On the other hand a fairly wide choice of liquid equilibrium vapour pressure data can be sourced in addition to sublimation for similar examples that have relatively few terms for testing in their defining equations.

Simplifying the defining conditions is recommended and in line with other physical approximations means for example real gases are taken in a range where ideal gas behaviour can be assumed. Again to keep the equation form as simple as possible a pressure limit that a vapour might reach is selected to be the same as the standard pressure of 1 bar.

References

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