

Thermodynamic modelling of reactions in materials chemistry

Ian Brown

Callaghan Innovation & the MacDiarmid Institute, Lower Hutt, New Zealand
(email: ian.brown@callaghaninnovation.govt.nz)

Keywords: *thermodynamics, ceramics, metallurgy, carbothermal reduction*

Thermodynamics and solid state reaction studies

In planning and undertaking any study involving reaction chemistry across the broad field of solid state materials, there are two simple questions to address: will this reaction proceed and can it proceed to completion under the planned conditions? To address these questions we must examine the effect of two major factors that control all chemical reactions – including those that determine outcomes in solid state chemistry – thermodynamics and kinetics. For many researchers, the study of thermodynamics is something undertaken in student years in physical chemistry course work. The principles and indeed many of the key equations that define the four laws of thermodynamics are tucked away in our heads and textbooks and these have been laid out and examined in legions of publications for over 100 years. This is not the forum to reproduce or review these underlying principles. The goal of this brief monograph is to demonstrate how thermodynamic analysis, using these simple principles and commonly available software, is a powerful analytical tool to complement observational studies we may undertake using the more usual experimental markers of the progress of a reaction, such as X-ray diffraction, thermal analysis and evolved gas analysis.

In 1875 Josiah Gibbs proposed that enthalpy, temperature and entropy could be expressed as a single quantity, now known as the Gibbs Free Energy of reaction ($\Delta G = \Delta H - T\Delta S$). The Gibbs Free Energy remains our principal guide to the state of equilibrium or completion of any given reaction. The value of ΔG can also predict the direction of the chemical reaction under conditions of constant temperature and constant pressure. If ΔG is positive, the reaction requires external energy to occur and if it is negative, then it occurs without external energy input (it is spontaneous).

In this study the commercially available software HSC Chemistry¹ is used to examine how the Gibbs Free Energy can support our understanding and prediction of the outcome of solid state reactions in simple inorganic systems and in more complex ceramic and metallurgical processes.

Inorganic systems – the decomposition of calcite

The lime-limestone equilibrium is one of mankind's earliest industrially significant chemical reactions, with lime use in agriculture, cementing and glass making well documented for millennia. Recent work at Callaghan Innovation^{2,3} has shown viable chemical engineering routes for using this process (known somewhat inaccurately as

'calcium looping') as the basis for a sustainable CO₂ capture mechanism for flue gases from thermal power plants, cement works and the like. The equilibrium reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ provides a good test of thermodynamic modelling and enables examination of responses to changes in the mole ratios of reactants, temperature and pressure.

Fig. 1 shows the equilibrium data for one mole of CaCO₃ decomposing in an atmosphere of one mole of argon gas at a fixed pressure of 1 bar. The graph shows the reaction commencing above 450 °C and concluding above 1200 °C. The equilibrium temperature where moles of CaCO₃ and CaO are equal is 817 °C.

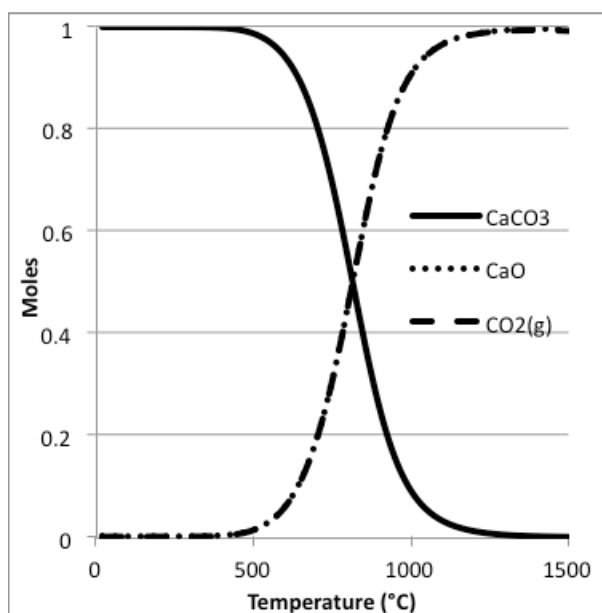


Fig. 1. Reaction equilibrium for $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$, 1 mole calcite, 1 mole argon.

Fig. 2 shows the effect on the equilibrium of changing the gas environment by undertaking the experiment in 100 moles of argon, but still at 1 bar pressure. The cross-over point for the equilibrium shifts significantly down in temperature to 617 °C. To undertake this calculation the model assumes that all reactants and products are confined in a single reaction vessel. What we learn is that by substantially reducing the partial pressure of CO₂ in this hypothetical reaction vessel the free energy for the reaction is significantly lowered. Effectively, we are simulating a flow reactor by progressively diluting the evolved CO₂ product gas and forcing the chemical equilibrium strongly from reactants towards products. An alternative way to model the equilibrium is to maintain a constant mole ratio of reactants but change the pressure that the model reaction vessel is subject to.

Fig. 3 shows the effect of reducing pressure on the de-

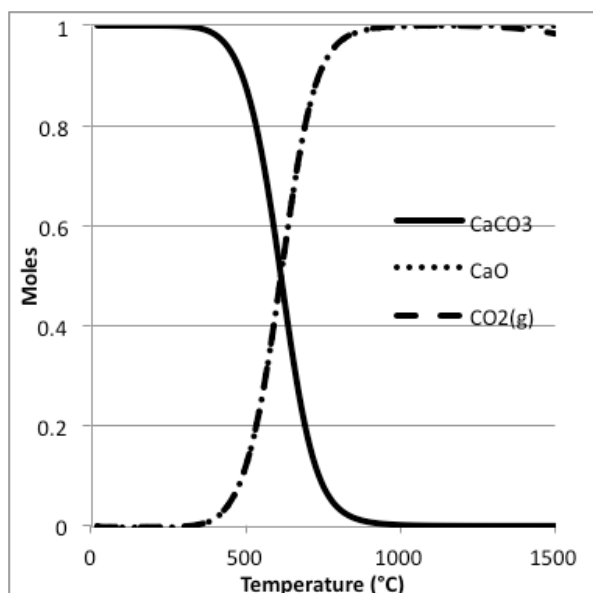


Fig. 2. Reaction equilibrium for $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. 1 mole calcite, 100 moles argon.

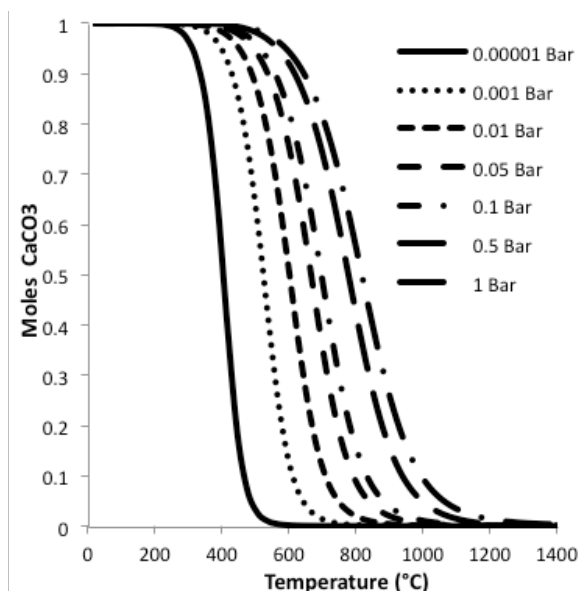


Fig. 3. Mass change for CaCO_3 decomposition under vacuum.

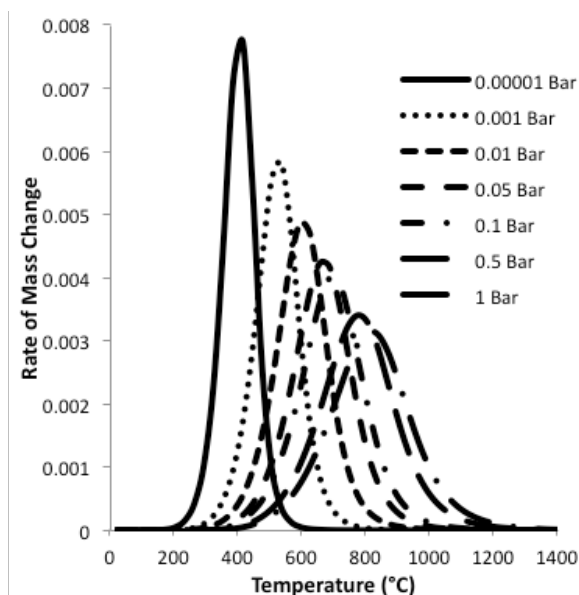


Fig. 4. Rate of mass change for CaCO_3 decomposition under vacuum.

composition profiles for calcite for the fixed molar ratio used in Fig. 1, namely 1 mole CaCO_3 and 1 mole argon. Effectively this is modelling a thermogravimetric analysis experiment of calcite decomposition. Taking this further, by applying a differential model (in this case a simple moving average) to the calcite deposition data curves we can generate the equivalent of a differential thermal analysis curve for each mole ratio/pressure condition. This is shown in Fig. 4.

The final thermodynamic analysis to examine for this equilibrium reaction is to quantify the effect of increasing the CO_2 partial pressure on the equilibrium. Thermodynamic laws would predict that increasing the CO_2 partial pressure will inhibit the reaction, delaying the onset of reaction and shifting the maximum rate of reaction to higher temperatures. Although this is borne out by examination of Fig. 5, the extent of inhibition of the reaction is at most some 30 °C and this effect saturates rapidly beyond 10 moles of additional CO_2 in the reaction environment. The effect of reduced pressure (Figs. 3 and 4) on the decomposition chemistry is much more substantial than the effect of increased pressure.

Having completed a comprehensive study of the thermodynamic behaviour of calcite decomposition under a diverse range of atmosphere conditions it is very informative to compare this data with real experimental data. In this case a well crystallised and well characterised calcite powder has been analysed by differential scanning calorimetry (DSC) under air, argon, nitrogen and CO_2 atmospheres over the temperature range from ambient to 1000 °C at 10 °C/min.

Fig. 6 shows the normalised calcite weight loss curves. It can be seen that both static and flowing environments of *non-participating* gases (air, N_2 , Ar) result in a very tight data cluster with less than 20 °C separating the points of maximum rate of weight loss (Static Air: 754 °C; Flowing Air: 762 °C; Flowing N_2 : 758 °C; Flowing Ar: 743 °C). Cross-referencing to Figs. 3 and 4 indicates that the equivalent atmosphere seen by the calcite material is 0.25-0.35 bar pressure. The CO_2 result is very different indeed, being a *participating* gas in the reaction chemistry. Even at the relatively low gas flow rates used in these experiments the reaction is greatly inhibited, with the temperature at the point of maximum rate loss being 933 °C. Given that Fig. 5 shows that the maximum rate of weight loss at 1000 bar CO_2 pressure is 885 °C, this gives us some idea of the extent to which diffusion barriers in the surface regions of the calcite grains are repressing this reaction. This is a good example of the extent to which kinetic factors can dominate over thermodynamic factors in determining product outcomes in some chemical equilibria.

Ceramic systems – silicon nitride synthesis by carbothermal reduction of silica

Silicon nitride (Si_3N_4) is a non-oxide ceramic, with a three dimensional covalent structure built up by corner-sharing SiN_4 tetrahedra. This material is an important high performance technical ceramic with high hot hardness, thermal shock resistance and fracture toughness. Silicon nitride-

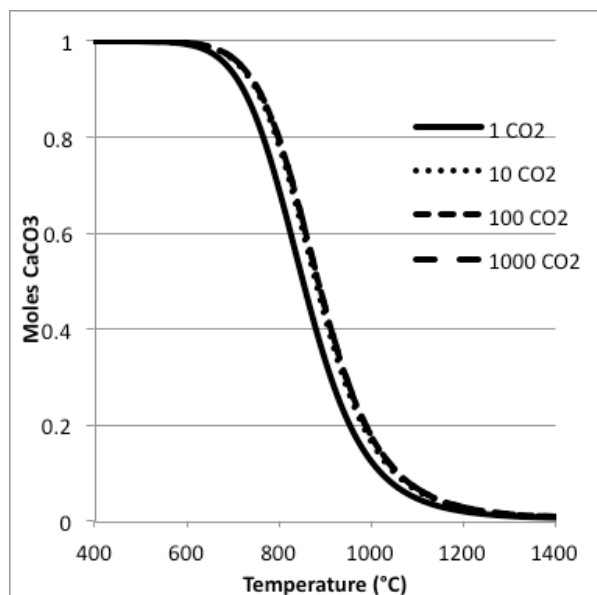


Fig. 5. Mass Change for CaCO_3 decomposition under CO_2 pressure.

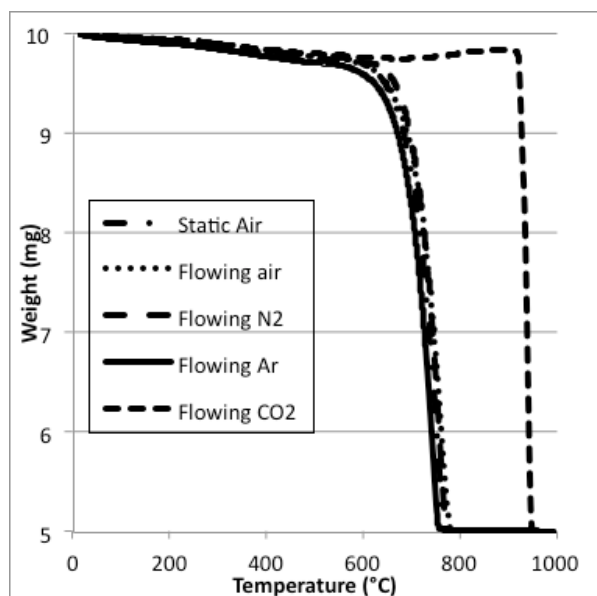


Fig. 6. Experimental DSC data for CaCO_3 decomposition under different atmospheres.

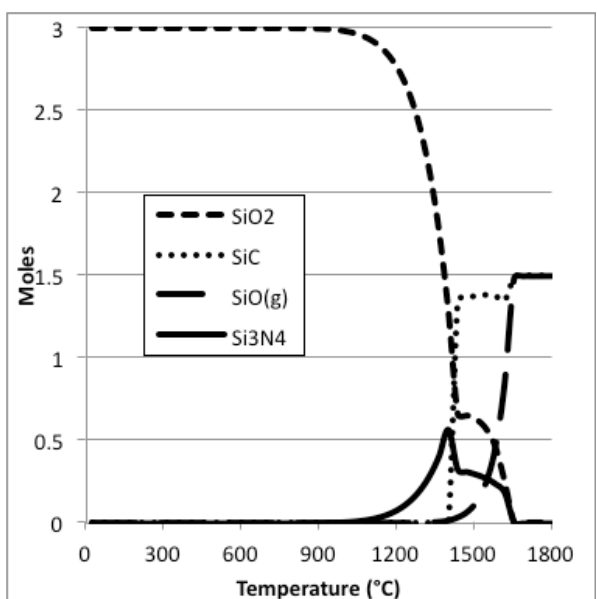


Fig. 7. Carbothermal reduction of SiO_2 to form Si_3N_4 under 10 moles N_2 .

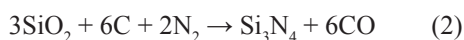
based cutting tools can cut cast iron, hard steel and nickel-based alloys with surface speeds up to 25 times faster than those obtained with tungsten carbide tools and are now used in considerable numbers to machine cast iron in the automotive industry and nickel superalloys in the aerospace industry.

One way to synthesis Si_3N_4 is to directly react the elements at elevated temperature:



Thermodynamic analysis shows that this reaction is highly exothermic with a strongly negative Gibbs free energy of reaction. While this sounds an ideal driver for completing the ceramic reaction, the reality is that this exothermic reaction is capable of generating sufficient heat to cause thermal runaway during the reaction. This can raise the reaction temperature above the silicon metal melting temperature of 1417 °C and create serious phase segregation through formation of agglomerates of molten Si droplets before the nitridation reaction has had time to achieve completion.

A different approach to silicon nitride formation is to reduce silicon dioxide ('silica') with carbon under a nitrogen atmosphere. This process is known as carbothermal reduction:



In this case, analysis reveals that the Gibbs free energy does not become negative until above 1550 °C, at which point the enthalpy of the reaction is +1170 kJ. Having gas-solid reactants with gas-solid products allows plenty of variables to help manage and control this strongly endothermic process chemistry. Our first model fixes the silica and carbon levels at their molar levels in reaction 2 while varying the nitrogen content. What we find is that the molar volume of CO product gas (6 moles CO vs the 2 moles of reactant N_2) will effectively repress this reaction until such time as a substantial molar excess of nitrogen is achieved. Figs. 7 and 8 show the equilibrium for 10 and 15 moles of nitrogen respectively. The data show that even this large nitrogen excess is still insufficient to allow synthesis of the theoretical level (1 mole) of Si_3N_4 . This level is not achieved until over 20 moles of nitrogen are used, an excess of 10 times the stoichiometric requirement. Figs. 9 and 10 show the equilibria calculated for 30 and 100 moles of nitrogen, respectively. It can be seen that at least 30 moles of nitrogen are required to generate a sufficiently wide synthesis temperature window for Si_3N_4 stability that would enable the practical and successful synthesis of phase pure silicon nitride.

A closer examination of these equilibrium data curves reveals an unexpected challenge. At the upper end of its stability window the Si_3N_4 product is thermodynamically unstable with respect to silicon carbide (SiC) and silicon monoxide (SiO). In Figs. 8-10 these two phases overlay one another. The latter phase is a particular problem due to its volatility. In a real reaction experiment under flowing nitrogen, the very same drivers that indicate that we should increase the nitrogen flow rate to reduce the partial

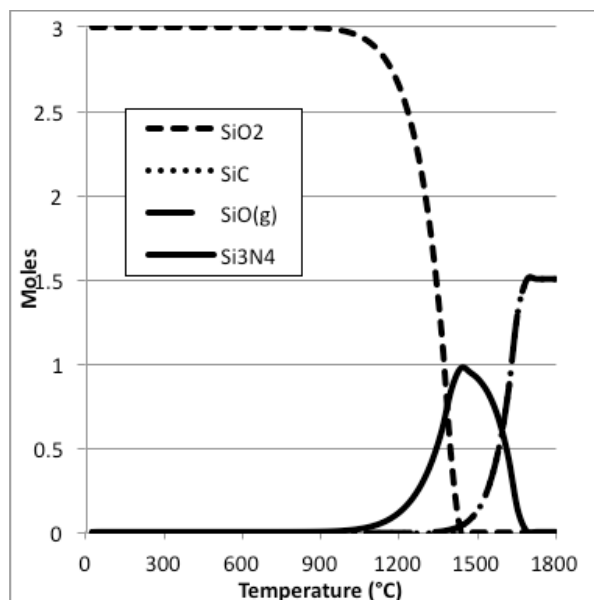


Fig. 8. Carbothermal reduction of SiO_2 to form Si_3N_4 under 15 moles N_2

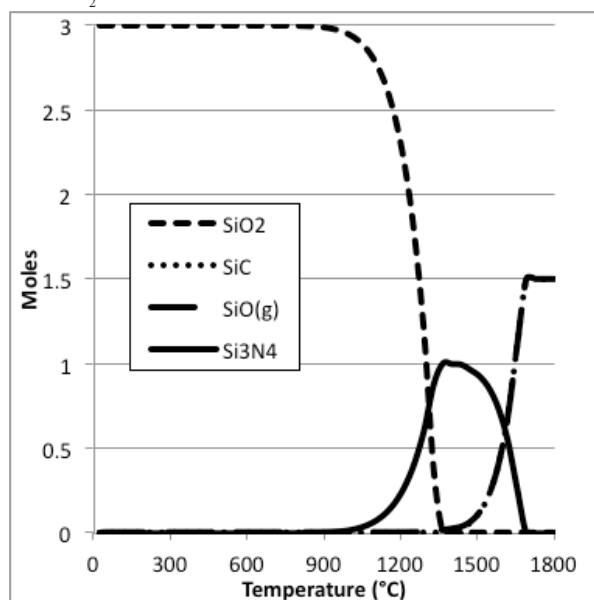


Fig. 9. Carbothermal reduction of SiO_2 to form Si_3N_4 under 30 moles N_2 .

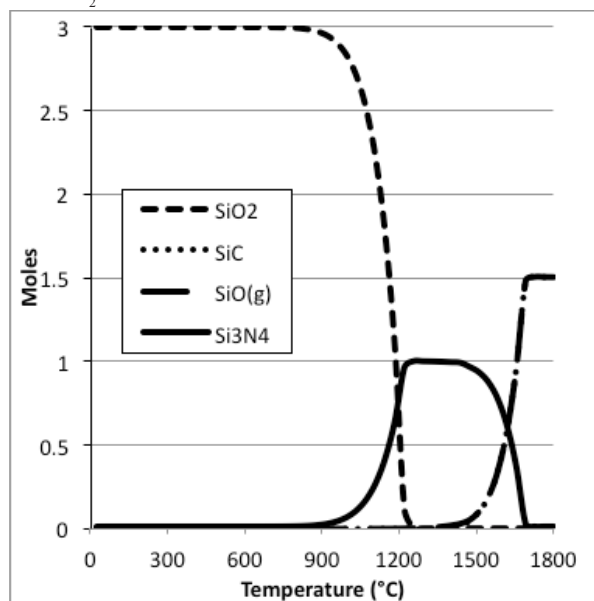


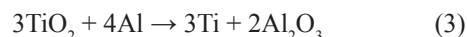
Fig. 10. Carbothermal reduction of SiO_2 to form Si_3N_4 under 100 moles N_2 .

pressure of CO will also cause this volatile SiO phase to be removed, forcing the Si_3N_4 to decompose to SiC and SiO more quickly. This is a reaction system where compromise and careful optimisation is required to obtain phase pure Si_3N_4 product.

Metallurgical systems – reduction of titanium dioxide to titanium metal

Titanium has the highest strength to weight ratio of any metal. Methods for the manufacture of this high durability, high value metal are complex multistage processes often proceeding from the titanium ore rutile (TiO_2) via a TiCl_4 intermediate followed by reduction with reactive metals such as magnesium or sodium. The long-established Kroll process (1940)⁴ and the more recent Armstrong process (1998)⁵ use Mg and liquid Na respectively. Can thermodynamic analysis show us an alternative process route? Fig. 11 shows the Gibbs free energy for the reduction of titanium dioxide (titania) to form titanium metal using a range of reductants known to break metal–oxygen bonds.

It is clear from the data that well known reducing agents such as hydrogen and carbon are unable to reduce the strong Ti–O bonds to Ti metal under conventional temperature/pressure/time conditions. There is no temperature regime where the free energy for the reaction is negative, so the reaction cannot proceed spontaneously under any defined T–P–t conditions. Also shown are data for three metal reductants, aluminium, magnesium and calcium where the ΔG curves are strongly negative at all temperatures below 2000 °C. That is, there is a strong thermodynamic driver for the reduction to proceed. Some years ago researchers at the University of Waikato developed a titanium synthesis route based on Al metal reduction of titania.^{6,7} A study of the drivers for this reaction provides a good exemplar for the role of thermodynamics in guiding reaction paths in process metallurgy. Consider the reaction:



This reaction is usually undertaken in an argon atmosphere to eliminate all risk of oxidation of either the reactants or products. The ΔG vs temperature data for this reaction is shown in Fig. 11, indicating a ΔG value of less than -100 kJ at all temperatures of interest. So our immediate expectation is that this reaction should proceed. Reality is different. The product formed when using the above stoichiometry is consistently a TiAl intermetallic phase. So what is wrong – has our modelling failed? The simple answer is the model works and we have leapt ahead without undertaking due diligence on the essentials of the analysis. Fig. 12 shows the mole fractions of reactants and products formed when 3 moles TiO_2 and 4 moles Al achieve equilibrium under argon.

The thermodynamic stability of the intermetallic phases AlTi and Al_3Ti is greater than that of pure Ti (the Gibbs Free Energy is more negative), so much of the reactant Al metal has associated with the intermetallic phases and has not been made available to reduce the TiO_2 beyond TiO. Fig. 13 shows the result of re-calculating the equilibrium

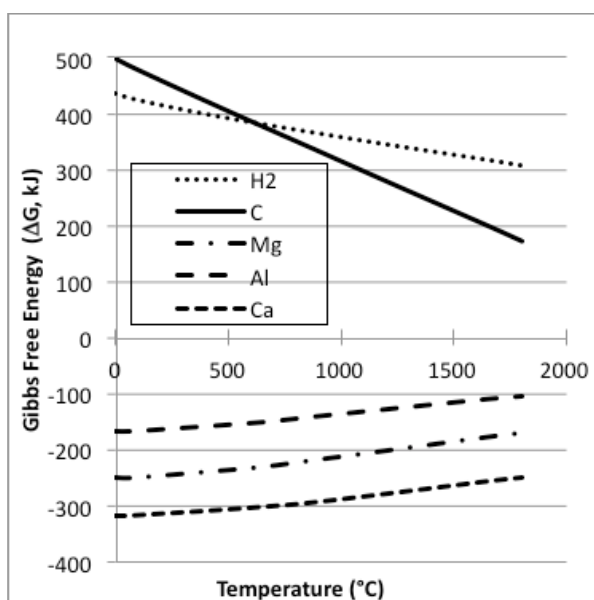


Fig. 11. Gibbs Free Energy as a function of temperature for TiO_2 reduction.

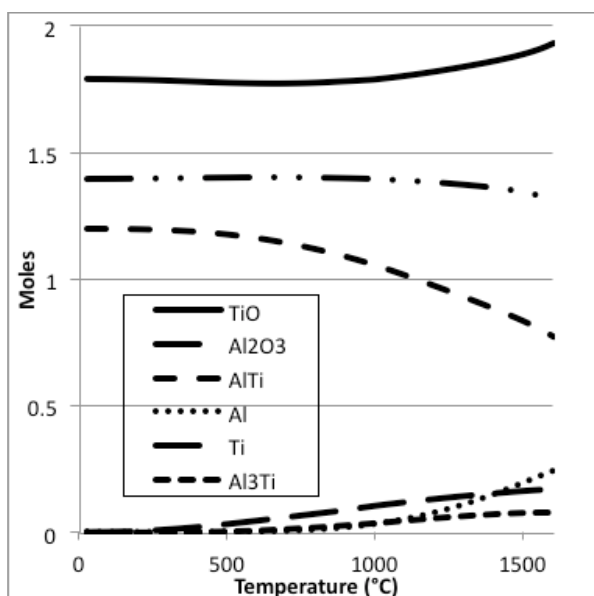


Fig. 12. Equilibrium mole fractions for the reaction $3\text{TiO}_2 + 4\text{Al}$ in argon.

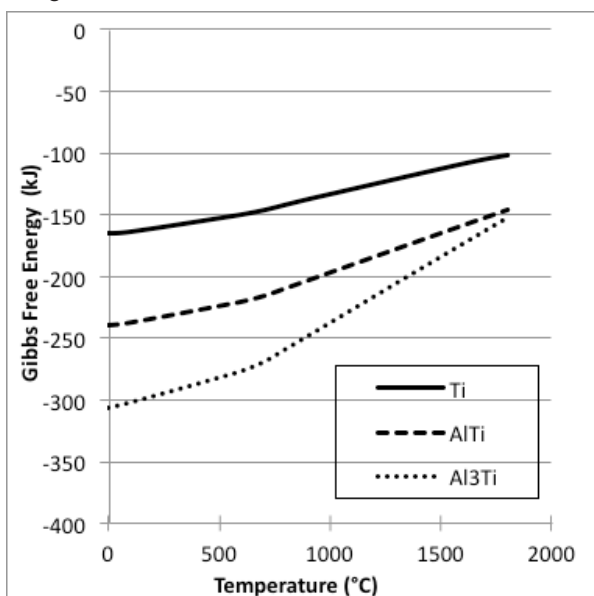


Fig. 13. Gibbs Free Energy as a function of temperature for Al reduction of TiO_2

using an excess of Al metal. The extent of the excess determines the ratio of AlTi to Al_3Ti in the products. The ΔG data can be recalculated based on stoichiometric formation of AlTi or Al_3Ti , using the equations:



Fig. 13 shows ΔG data for reactions 4 and 5 shown alongside that for reaction 3. At lower temperatures Al_3Ti formation is strongly favoured but the free energy gap to AlTi closes at elevated temperatures. This Al reduction path for the synthesis of pure Ti metal is not favoured thermodynamically. Instead we have a novel path to synthesise Al-Ti intermetallic phases by controlling TiO_2/Al mole ratio and temperature to selectively form AlTi or Al_3Ti phases. Using this reaction path design in a practical process requires removal of the contaminant oxide phase, in this case Al_2O_3 , from the product mixture. The removal of contaminant oxide phases will also be a feature of reduction reactions using other reactive metals, including Mg, Ca and Na. This goes some way to help explain why many of the current commercial synthesis routes proceed via TiCl_4 intermediates, as the removal of contaminant chloride salts may have more appeal than removal of oxide phases in a production process. Nevertheless, the TiO_2/Al reduction methodology developed at Waikato remains a valid path to synthesise high value intermetallic phases for the metallurgical industry.

Summary

Thermodynamic analysis can be applied across a wide range of reaction systems in solid state and materials chemistry. Researchers draw immense value from being able to predict whether a reaction can proceed, which reaction path and product set is preferred and which reaction intermediates may be encountered. However, as in every field of research, there are traps for the unwary and thermodynamic analysis has plenty, sufficient to warrant a brief examination:

The data: The quality of the modelling is only as good as the quality of the data used to compile the databases. The thermodynamic properties of many materials have been exhaustively measured and have been collated in a number of databases, e.g. Barin,⁸ Janaf,^{9,10} that have subsequently been drawn into software packages such as HSC Chemistry¹ and Thermocalc.¹¹ The database managers attempt to grade the quality of these data sets on the basis of the perceived experimental rigour of the measurement. Most commonly the data are derived by fitting heat capacity (C_p) vs temperature data to an established, albeit empirically derived, equation of state algorithm (known as the Kelley equation).¹² In some cases C_p data for chemical compounds which are absent from the databases can be found in current literature and most modern thermodynamic analysis software has options to enable users to readily integrate this new data into a working database.

The closed vessel model: The process for calculating the species present at chemical equilibrium places all reactants and products in the same closed space. In modelling

a reaction where gas species form part of the chemistry, such as in the calcite decomposition or carbothermal reduction of silica examples given previously, the model conditions (moles of reactant, moles of carrier gas, system pressure) can be varied to simulate the conditions that would be encountered in a real flow reactor. In the real experiment the gas species may be removed from the reaction environment prior to equilibrium being established.

Kinetics: While thermodynamics provides the first filter for assessment of likely reaction paths and outcomes, the kinetics of any given reaction provide a second filter that may dramatically delay or temperature shift the progress of a reaction that might otherwise be expected to proceed readily. It must be understood that even drivers such as a strongly negative Gibbs free energy may not be sufficient to enable a reaction to go to completion in the temperature window that the thermodynamic model may indicate. The time frame to achieve equilibrium cannot be drawn from these models. The nitridation of silicon metal [reaction (1)] is a good case in point. The model shows highly negative ΔG and ΔH data at all temperatures above ambient and yet this highly exothermic reaction does not commence until well over 1000 °C because a very thin native oxide skin on the Si metal surface acts as a kinetic barrier, imposing diffusion control where perhaps none might have been expected.

Thermodynamic modelling can complement classic analytical techniques to assess the state and path of many solid state reactions. It cannot assess the rate of such reactions, so an 'eyes wide open' approach is vital in our interpretation of the modelling outcomes. A good dose of chemical common sense in combination with the knowledge of

how to draw best value from thermodynamic modelling and software packages offers researchers a highly effective and little used chemical research tool.

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