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Tying up loose ends

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Abstract

This, the 300th edition of *Thermochimica Acta* coincides neatly with the retirement of the author. It is an opportune moment to look back at research which has featured the use of classical calorimetry and thermal analysis to investigate such disparate areas as organic and organo-metallic compounds on the one hand, and pyrotechnic systems on the other. This retrospective view is concerned in part with some of those issues that are as yet unresolved. © 1997 Elsevier Science B.V.

Keywords: Calorimetry; Heat capacity; Organic; Organo-metallic; Pyrotechnics

1. Introduction

A number of readers may recognise the title as part of the last sentence of a presentation at the conference on the stability of explosives held in Sweden in 1995 [1]. It is particularly apt now since this paper marks not only the 300th edition of *Thermochimica Acta*, but also the retirement of the author. It provides an excuse for a retrospective look at areas of research which have been of interest to the author over the last 30 years and to cast an eye over some of the loose ends which remain.

Classical calorimetry and thermal analysis (differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) are the recurrent themes. The last 30 years have seen a remarkable turnaround in the fortunes of classical thermochemistry and thermal analysis. From the perspective of determining well-defined thermodynamic quantities, thermal analysis, with its *apparent* lack of thermodynamic rigour, has been regarded as the poor relation of classical thermochemistry. Nevertheless, over this period thermal analysis has flourished whereas interest in classical calorimetry has declined and there are now few remaining centres of excellence. Thermochemical information underpins much technological progress and it would be unfortunate if the ingenuity in design of both equipment and experimental technique should be lost.

The growing disparity in interest is understandable: in contrast to classical calorimetry where instrument development has often been one-off, thermal analysis has a competitive manufacturing base and instruments are suited to the study of a wide variety of problems. The recent innovative use of complex temperature programmes in place of linear temperature ramps is set to establish new horizons [2]. An additional benefit has been the renewal of interest in the operational theory of DSC. It is likely to be the nemesis for the claim to simplicity which has been something of a

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disservice to the technique. For too long, there was an emphasis on a single experiment to solve what were often complex kinetic problems.

2. Full circle: Organo-halides, pyrotechnics and back again

The author's introduction to classical calorimetry was through a study of organo-halide compounds [3]; the most recent work, some 30 years on, has also been a study of organo-halide compounds [4]! The former was the first project undertaken after joining the thermochemical group at Leeds. Adiabatic calorimetry was used in a reaction scheme devised by Carson et al. [5] in which the organo-halide was reduced by $LiAlH_4$ to the corresponding alkane. The latter made use of aneroid rotating combustion calorimetry, where organo-iodine compounds were burnt in the presence of aqueous KI solution to dissolve the iodine produced in the combustion. A comparison experiment was designed with benzoic acid, iodine and KI solution with the object of linking the energy of combustion of the organo-iodine compound to that of benzoic acid. What is surprising is that there are still calorimetric values today which owe their origins to measurements made early in the century before the need for corrections to thermodynamic standard states was fully appreciated. The determination of the enthalpy of formation of CH_2I_2 was a case in point where Berthelot's [6] value was updated [7]. The critical evaluation of thermochemical data is becoming increasingly important in view of the decline in experimental work. The recent publication by Pedley [8] relates the enthalpy of formation to structure in order to correlate enthalpies in the gaseous and condensed states. The available data for some organo-halides were summarised in Ref. [4]. Of course, critical evaluations of data always prompt a sideways glance at the standing of one's own measurements! During the intervening period, between the first and last investigations into organo-halides, a number of different compounds have been studied using a variety of calorimetric techniques, most prominent being organo-metallic compounds of germanium and tin by combustion calorimetry.

Interest in thermal analysis came with the purchase of a Perkin–Elmer DSC 1b, ostensibly to produce ancillary information on purity and heat capacity required for combustion calorimetry. A valuable spin-off was the study of self-sustained solid-state combustion which complemented gas-phase combustion studies in progress at that time in the Department at Leeds. The application of thermal analysis to pyrotechnic systems represents only a small area of activity but one which has proved to be of inestimable value. Under ignition conditions, analysis is limited to the determination of ignition temperatures but has led to a general exploration of the effect of composition on ignition characteristics. Under non-ignition conditions, the primary aim is to identify the reaction stages and here complementary techniques have an important role to play. A note of caution! Results obtained by thermal analysis are relevant to the conditions of the experiment but these are far removed from those which exist in the combustion regime.

3. Thermal environment: Heat-capacity measurements

DSC in the hands of the experienced practitioner has the potential for producing thermochemical information of sufficient reliability for many purposes, with the advantage that measurements are not usually time-consuming. A case in point is the measurement of heat capacity where the principles have been established for many years [9]. However, practical problems become inordinately difficult where a highly precise measurement is required. Results approaching the precision of classical calorimetry can be obtained under favourable circumstances. A perfect example is the meticulous heat-capacity measurements by Callahan et al. [10]. In this instance, the calibrant had similar thermal properties to the samples, could be used in the same configuration in the DSC experiments and had a heat capacity determined by independent measurements traceable to international standards. Even so, the authors point out that, unless special circumstances prevail, the complexity of the experimental protocol makes measurements by DSC a poor option.

Our measurements of the heat capacity of C_{11}–C_{17} alcohols represent the first of the loose ends. The objective was twofold: to provide data in support of a programme of work on the extrapolation of vapour

Table 1
Tentative heat-capacity results summarised in the form $C/\mathrm{J\,K^{-1}\,mol^{-1}} = a + bT + cT^2 + dT^3$ for the temperature range T = (320–420) K

Compound	$a/(\mathrm{J\,K^{-1}\,mol^{-1}})$	$b/(\mathrm{J\,K^{-2}\,mol^{-1}})$	$c/(\mathrm{J\,K^{-3}\,mol^{-1}})$	$d/(\mathrm{J\,K^{-4}\,mol^{-1}})$	std.dev
1-Undecanol	9451	−77.99	2.217×10^{-1}	-2.061×10^{-4}	5.36
1-Dodecanol	−189.5	1.404	5.667×10^{-3}	-1.148×10^{-5}	5.44
1-Tetradecanol	2032	−16.01	5.309×10^{-2}	-5.394×10^{-5}	7.76
1-Hexadecanol	6878	−54.50	1.545×10^{-1}	-1.422×10^{-4}	15.2
1-Heptadecanol	−12715	102.4	-2.612×10^{-1}	2.231×10^{-4}	10.2

pressures to low temperatures, where the heat capacity measurements are used to obtain the temperature dependence of the enthalpy of vaporisation and to examine modifications to the theory of heat capacities of hydrogen bonded liquids [11]. There are examples of successful measurements of the heat capacity of liquids: Banipal et al. [12] used a Setaram C80 calorimeter with a cell which allowed measurements to be made in the absence of a vapour phase above the sample. Our results were obtained using a Perkin–Elmer DSC 4 with the samples sealed in high-pressure crucibles to ensure that any mass loss during the measurements was negligible. However, our results lacked reproducibility between different sets of measurements. Each set reproduced the general shape of the heat-capacity results as a function of temperature, but gave rise to absolute differences often amounting to 3–4%. This lack of agreement between otherwise satisfactory results is particularly frustrating and underlines the difficulty of reproducing exactly the thermal environment needed for precise measurements. The same difficulty can arise in establishing standard test methods and may lead to a lack of conformity between the results from different laboratories. The heat-capacity results are summarised in Table 1.

4. Sample preparation: Calorimetry of organo-compounds of germanium, tin and lead

Another loose end is associated with classical calorimetry, not with the calorimetry itself but with the difficulty encountered in the preparation of sufficient sample with a high enough purity to make calorimetry a feasible proposition. The determination of bond strength has been the primary aim of our calorimetric studies of organo-metallic compounds. The elements germanium, tin and lead are of particular interest because of the increasing metallic nature from germanium to lead and their presence in the same periodic group as carbon. The determination of bond enthalpies or bond dissociation enthalpies requires gas-phase data in order to eliminate the effects of cohesive forces between molecules. The aneroid combustion calorimeter and the Knudsen effusion apparatus used in our studies, and the results obtained thereof, have been reviewed by Carson [13]. The small energy equivalent of the aneroid calorimeter means that smaller quantities of samples may be used than in a conventional calorimeter: an important consideration for samples difficult to prepare or liable to detonate under a high pressure of oxygen. Even so, the preparation of suitable samples remains a major stumbling block, particularly with large molecules. Here, the enthalpy of formation is a relatively small quantity obtained from the difference between large enthalpies – of combustion and of the formation of CO_2 and H_2O.

The combustion calorimetry of germanium, tin and lead compounds shows contrasting features. With organo-tin compounds, combustion using static calorimetry has proved to be very successful. With organo-germanium compounds there is some uncertainty in the precise form of the GeO_2 produced in the combustion. This uncertainty may be eliminated by using rotating combustion calorimetry, whereby the GeO_2 is dissolved in a suitable solvent. The method as devised by Bills and Cotton [14] used aqueous HF solution, whereas in our measurements we have used aqueous KOH solution.[15]. With a suitable comparison experiment the enthalpy of formation may be linked to the enthalpy of formation of hexagonal GeO_2, with the further advantage that the Washburn corrections are minimised. There is something very satisfying in devising reaction schemes, where corrections are eliminated and the results linked to well-established calorimetric data. Rotating combustion is essential for organo-lead compounds which burn to give a mixture of products in different oxidation states. Scott et al. [16] linked the enthalpy of formation to that of $Pb(NO_3)_2$. In our experiments, the link was to the enthalpy of formation of PbO_2 [17] and a subsequent investigation [18] using solution calorimetry established a link between the enthalpy of formation of $Pb(NO_3)_2$ and that of PbO_2.

Bond dissociation enthalpies of the germanium and tin compounds have been discussed by Carson [13]: the absolute values of the dissociation enthalpies are often unreliable because of large uncertainties in the enthalpy of formation of the radicals. The effect of these uncertainties may be eliminated by an astute choice of comparisons. For example, in a comparison between the dissociation enthalpies $D\{Ph_3Sn - Ph\} = 274\,kJ\,mol^{-1}$, $D\{Ph_3Sn - C_2H_3\} = 282\,kJ\,mol^{-1}$ and $D\{Ph_3Sn - C_2Ph\} = 427\,kJ\,mol^{-1}$, the uncertainty ($\approx$21 kJ mol^{-1}) in $\Delta_fH^{\ominus}(Ph_3Sn)$ is of no consequence and it is possible to detect unexpected bonding characteristics. The bond dissociation enthalpy in Ph_3SnC_2Ph is ~60 kJ mol^{-1} greater than the difference expected between $D\{Sn - C(sp)\}$ and $D\{Sn - C(sp^2)\}$ ($\approx$80 kJ mol^{-1}). The same effect is found in the corresponding Ge ethynyl compound and points to interaction between the π-electrons of the triple bond and unfilled orbitals on the tin and germanium atoms. Fig. 1 shows the remarkable parallel which exists between the bond dissociation enthalpies of tin and germanium.

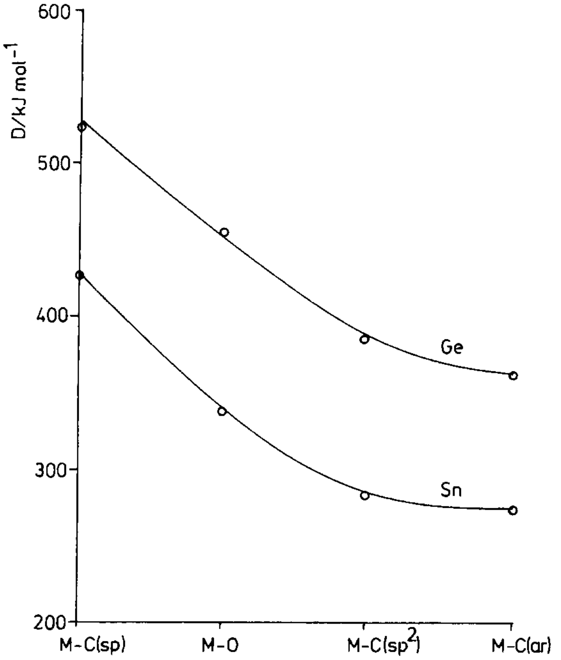

Fig. 1. Dissociation enthalpies for some germanium and tin bonds.

There is sufficient experimental information on organo-germanium and organo-tin compounds to construct a self-consistent bond enthalpy scheme. The terms based on the Laidler parameters quoted by Cox and Pilcher [19] have been used by Carson [13] to investigate the presence of strain in the 1,1-diphenylstannocyclopentane, 1,1-diphenylstannocyclohexane and 1,1-diphenylgermanocyclopentane molecules. The approach is illustrated in relation to the first of these compounds. The enthalpy of atomisation is represented by the contributions,

$$\Delta_aH^{\theta} = 2\Delta_aH^{\theta}(Ph) + 2E\{Sn - C(ar)\} + 2E\{Sn - C(sp^3)\} + 3E\{C(sp^2) - C(sp^2)\} + 8E\{C(sp^3) - H\}_s$$

A comparison is then made between this value and the value calculated from the experimental enthalpy of formation. In the present case, the discrepancy between the two values indicates that the molecule is strained to the extent of ~54 kJ mol^{-1}. This may be explained by including the strain energy usually associated with 5-member rings and the influence of steric hindrance between the phenyl groups on $E\{Sn - C(ar)\}$. Surprisingly there appears to be no significant difference between the strain in the 5- and 6-member ring systems. The extensive information on the thermochemistry of germanium and tin compounds still hardly touches the known organic chemistry of these elements. Germanium, in particular, forms a remarkable range of ring compounds with carbon, both saturated and unsaturated, containing one or more germanium atoms [20]. An extension of the thermochemistry to these compounds represents a formidable task, even selecting only key compounds. The preparation of 5 g samples of > 99.9 mol% purity would be the starting point – no mean task!

5. The black art: Pyrotechnics

Turning now to the work relating to pyrotechnic systems, the central role of thermal analysis is in contrast to its ancillary function in the work on organo-metallic compounds, a role that was reviewed in this journal in 1987 [21]. Pyrotechnic systems have a critical part to play in many areas of application, both military and domestic. The formulation of the classical mixed-powder pyrotechnics was always described as 'a black art'. It was to the credit of early practitioners that they were able to develop working systems based on experience and intuition which were far in advance of contemporary understanding of the mechanism of combustion. Even today, with our much greater knowledge, it remains true that the development of alternatives to mixed powders outpaces our ability to offer a quantitative explanation of their behaviour in terms of anything approaching first principles. The investigation of pyrotechnic systems is notoriously difficult and is dogged by a dearth of information on physico-chemical properties. So, it has been almost inevitable that our work should have left as many loose ends as there have been satisfactory resolutions.

The research at Leeds has been concerned primarily with a study of the combustion regime which is a step removed from mainstream thermal analysis. The latter is largely directed towards the identification of reaction steps. It continues the innovative research in Japan and USA in the 1950s and 1960s, which set the pattern for future developments. The identification of reaction steps is one of comparison between the thermal analysis curves for the pyrotechnic mixture, the components and the likely intermediate mixtures complemented by a range of analytical techniques. X-ray diffraction, IR-spectroscopy and mass spectrometry have all been applied to the identification of intermediates and final products; combustion calorimetry has been used to investigate the stoichiometry of the combustion process. It has proved possible to link the self-sustained combustion process with the presence of reactions identified by thermal analysis.

Pride of place in *Thermochemica Acta*, page one of volume one, is a paper by Rogers and Smith [22] on the study of chemical kinetics by scanning calorimetry. Although the early promise may not have been fully realised, thermal analysis has been used widely to obtain information on the chemical kinetics of explosives, propellants and pyrotechnics. The determination of kinetic parameters by thermal analysis has always been contentious and with energetic materials there is a question of relevance: with pyrotechnic delay compositions, the activation energy is not consistent with the small temperature dependence of burning velocity typical of such pyrotechnics. A case in point is the composition $W/K_2Cr_2O_7$, where burning-velocity measurements lead to an activation energy of 42 $kJ\,mol^{-1}$ [23] in marked contrast to the value obtained by thermal analysis (239 $kJ\,mol^{-1}$) [24]. An alternative method for obtaining the activation energy of energetic materials is the measurement of times-to-ignition using a variety of experimental techniques. Nevertheless, it is important to establish the degree of supercriticality involved in the measurements to avoid misleading results [25].

The determination of kinetic parameters is often seen as an end in itself. However, a knowledge of chemical kinetics makes an important contribution to our understanding of the mechanism of chemical change. For energetic materials, the kinetic parameters may be linked to the ignition and burning characteristics, perhaps as part of thermal hazard evaluation. One direct method of obtaining information about the combustion process is by temperature profile analysis, a term which has been coined for the study of the temperature–time profile through the combustion wave. The basis of the technique is a description of the heat balance across a section of pyrotechnic. The key equation is:

$$\rho c(\mathrm{d}T/\mathrm{d}t) = \kappa(\mathrm{d}^2T/\mathrm{d}z^2) - h(T - T_a) + w$$

where T is the mean temperature, z the axial coordinate; ρ, c and κ denote the density, specific heat capacity and thermal conductivity, respectively, w the rate of heat evolution due to chemical reaction per unit volume, and $h(T - T_\mathrm{a})$ represents lateral heat loss. The theory ignores mass transport and is only applicable in its entirety to gasless pyrotechnic systems. It is the interpretation of w which leads to a description of the chemical kinetics. The technique was described in the 1950s by Klein et al. [26], Hill et al. [27] and Hill [28]. More recently, the general theory was elaborated by Boddington et al. [29,30] and the technique used to great effect by Brown and his co-workers (see, for example, Refs. [31–34]). The equation is crucial to the whole analysis. It is plausible, and experiments aimed at investigating its validity support its application at least within the limits of experimental error. The technique has been reviewed at a recent Royal Society meeting on Energetic Materials [35]. The activation energies obtained by temperature profile analysis typically lie in the (10–25) kJ mol^{-1} range; these values being an order of magnitude less than the results obtained by thermal analysis and consistent with a diffusion controlled process. The use of thermocouples to measure temperature profiles has limited the application of the technique to a maximum temperature of ~2000 K. Our attempts to extend the upper temperature limit using pyrometry merely exchanged one set of problems for another – from corrections for the finite size of the thermocouple to those for the spatial convolution of the pyrometer signal. The results obtained with conventional equipment, viewing the combustion normal to the axis of propagation, were unreliable but those from end-on measurements were much more successful [36].

The prediction of burning velocity of pyrotechnics has always been a much sought after goal. In view of the complexity of pyrotechnic reactions and the many factors which affect the burning velocity, a more realistic aim is to rationalise the empirical information available on burning velocities. Many numerical models for the combustion of pyrotechnics have been proposed over the years: Refs. [37] and [38], just two of the many, are representative of the major contribution from Russia to this area. Our emphasis has been on conceptual simplicity and ease of implementation [39]. The model is precisely the same as that which forms the basis of temperature profile analysis and is used to obtain the progress of the temperature wave through the pyrotechnic. In a sense, the approach examines internal consistency since the kinetic information needed to implement the model is derived from temperature profile analysis. However, the model may be used to investigate the propagation of the combustion wave under conditions not accessible to experiment. The model has been implemented assuming the pyrotechnic to be in the form of a column, one end at 2000 K and the other at 300 K. The boundary conditions can be varied to examine the ignition characteristics of the pyrotechnic when subjected to step-wise or linear temperature change. Fig. 2 shows the temperature wave developed when both ends of the pyrotechnic are subjected to the same

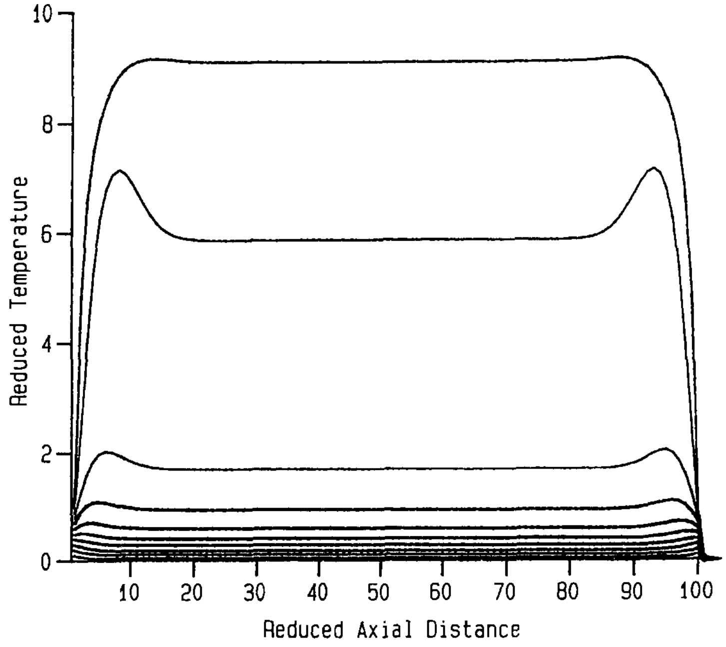

Fig. 2. Simulated thermal analysis experiment in which a sample of pyrotechnic is heated at 10 K min^{-1}, assuming no heat loss.

linear temperature rise under conditions leading to ignition. The temperature of the sample initially lags behind the programmed temperature but eventually rises rapidly to the combustion temperature. The model simulates an idealised thermal-analysis experiment under adiabatic conditions. The heating rate is 10 K min^{-1} and the sample size (the distance between the two boundaries) is 6 mm. An activation energy of 250 kJ mol^{-1} has been assumed. Attempts at tackling the inverse problem, to derive the activation energy from the dependence of ignition temperature on the rate of heating in a thermal analyser, have proved disappointing [40].

The transfer of combustion from one pyrotechnic to another is a key process in many practical devices. The numerical model should allow us to investigate the relative importance of the thermal properties of the donor and acceptor pyrotechnics. However, preliminary calculations predicted successful transfer in circumstances where experiments showed failure. A possible explanation was that the small activation energies derived from steady-state combustion gave rise to rates of reaction too large at low temperatures [36]. A solution is to assume a more complex rate law of the form,

$$k^{-1} = k_{\mathrm{Ar}}^{-1} + (BT^n)^{-1}$$

where k_{Ar} is the Arrhenius rate constant, $k_{\mathrm{Ar}} = A_{\mathrm{Ar}}\exp\,(-E_{\mathrm{Ar}}/RT)$, and B a diffusion coefficient. In the early stages, at low temperatures, the rate of reaction is determined by the Arrhenius term which leads to a rapid increase as the temperature rises until at higher temperatures the rate becomes less temperature-dependent and is determined by the diffusion term. The approach [24,32,36] offers the opportunity to rationalise the very different kinetic results obtained by thermal analysis and temperature profile analysis: thermal analysis leading to the Arrhenius term and temperature profile analysis to the diffusion term. An underlying problem in implementing the model is the lack of information on heat transfer and thermal diffusivity ($\kappa/\rho c$). For our measurements [41] of thermal diffusivity, we used the old-fashioned thermal analysis equipment with a large furnace. The method also uses large samples which for some mixtures would pose a safety hazard. A number of publications have described the use of thermal analysis to measure thermal conductivity following the early work of Brennan et al. [42]. However, there are reservations regarding the theory of the differential technique [43]. We have investigated alternative techniques using hot wire and laser-flash heating techniques, but neither have proved to be totally reliable. All these measurements are for temperatures far removed from typical combustion temperatures and the inevitable consequence is that values have to be estimated on the basis of the limited information available.

Table 2
Ignition temperatures determined by thermal analysis

Composition	T_{ign}/K
$W + K_2Cr_2O_7$	658
$W + KNO_3$	578
$W + K_2Cr_2O_7 + KNO_3$	553

The most recent pyrotechnic work at Leeds [1], concerned with ternary systems containing a metal and two oxidants, has presented the opportunity to tie-up some loose ends. The addition of a second oxidant to a binary system can significantly change the burning characteristics. In this way, it may be possible to engineer a pyrotechnic to meet a specific requirement. Alternatively, if unsuspected, the presence of a second oxidant may pose a safety hazard arising from a very much reduced ignition temperature. Table 2 lists the ignition temperatures of binary and ternary mixtures containing W, KNO_3 and $K_2Cr_2O_7$. They are linked to the melting temperatures of the individual and mixed oxidants. The study of ternary systems is nothing new with the emphasis on identifying reaction steps and linking the burning characteristics with composition.

Our interest lies in a different direction: we have attempted to account quantitatively for the consumption of the components as the temperature is raised. In principle, it should be possible to depict the changing amounts of the oxidants as a reaction pathway through the phase diagram of the mixed oxidant system. The calculations have been carried out for a step-wise temperature rise of 1 K every 6 s which simulates a thermal analysis experiment at 10 K min^{-1}. Inevitably, numerous assumptions have to be made. The analysis has been carried out for $W/KNO_3/K_2Cr_2O_7$, where we have information gained from thermal analysis experiments on the phase diagram of the mixed oxidants, and the stoichiometry and kinetics of reaction between the metal

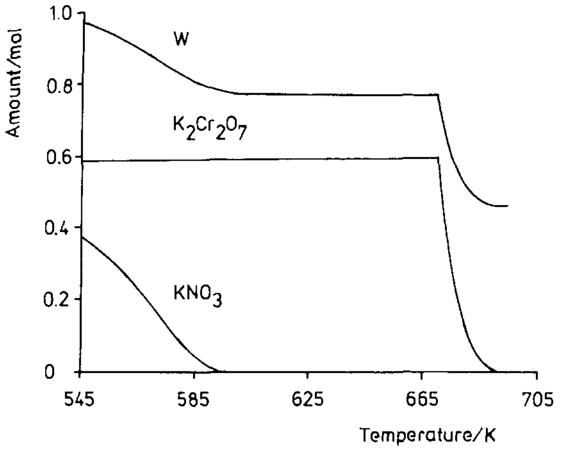

Fig. 3. Relative consumption of the components of a ternary pyrotechnic mixture of $W/K_2Cr_2O_7/KNO_3$ containing an excess of tungsten.

and the individual oxidants. It is assumed that the rate of reaction is negligible until the eutectic temperature is reached. The composition of the liquid phase is obtained from the phase diagram. The comparatively slow reaction between tungsten and $K_2Cr_2O_7$ means that this oxidant acts as a flux allowing the reaction between tungsten and KNO_3 to occur at lower temperatures than in the binary mixture. We have met with only partial success in our analysis, mainly because of the complicated nature of the reaction between tungsten and KNO_3. With mixtures containing an excess of $K_2Cr_2O_7$ compared with KNO_3 and an overall excess of tungsten, the results indicate preferential consumption of KNO_3 starting at 545 K, and continuing until ~595 K when it is entirely consumed. The pyrotechnic system effectively reverts to a binary mixture of tungsten and $K_2Cr_2O_7$ and reaction dies away until 670 K, the melting temperature of potassium dichromate. There is then a rapid reaction between tungsten and $K_2Cr_2O_7$. (Figs. 3 and 4). For these mixtures, at least, we have come full circle – in spite of all the assumptions the calculations are in agreement with the shape of the thermal analysis curves.

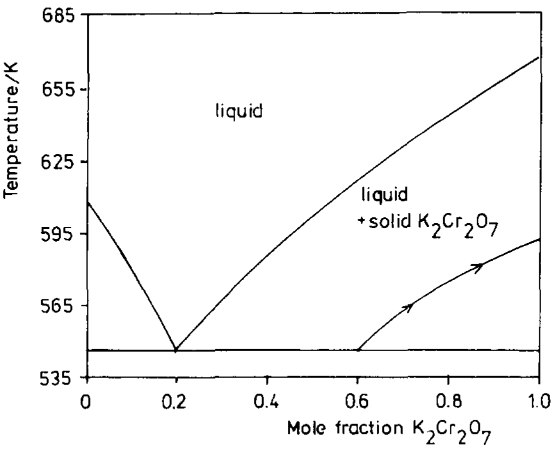

Fig. 4. Reaction pathway through the phase diagram of $K_2Cr_2O_7/KNO_3$ for a mixture containing an excess of tungsten.

6. For the future

Research over the last 30 years has left a trail of loose ends, some more enlivening than others. There is plenty to occupy another 30 years!

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This paper presents the opportunity to express my gratitude to my wife for her support and patience over the last 30 or so years and also to thank colleagues and ex-PhD students who have contributed so much to the successes – leaving aside the loose ends. Special thanks are due to T. Boddington, A.S. Carson and E.L. Charsley.

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