With compliments

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A Versatile Hot Stage Microscope

Lab studies in high temperature chemistry

The interpretation of phase diagrams is traditionally regarded by many students as a dull, abstract exercise. This is due, in most cases, to conceptual difficulties arising from an inability to visualize the realities of composition- and temperature-dependent constitutional changes, usually portrayed only as a series of two dimensional geometric figures.

The situation seems particularly unsatisfactory as far as high temperature phase equlibria are concerned. Because of the experimental complexity and the time involved, high temperature phase studies are not a usual feature of undergraduate laboratory instruction. In spite of the widespread interest in high temperature technology at the present time, many teaching establishments do not give to this aspect of inorganic and physical chemistry the emphasis that it deserves.

A chemistry course may be enriched by drawing attention to the practical implications of fundamental concepts, and it should be stressed at an early stage that a detailed knowledge of the internal structure of materials is necessary if their chemical and physical properties are to be fully understood or predicted. A receptive attitude in students may well be induced if their attention is drawn to interesting consequences of the high temperature reactions which crystals, melts, and glasses can undergo.

For example, the extraction of lithium metal from one of its most important sources, spodumene, $LiAl(Si_2O_6)$, is based upon a polymorphic transition which this structure undergoes at high temperature. The more open framework structure which is reconstituted from the low temperature chain lattice allows the Li^+ ions to become freely mobile in the channels, from which they are readily removed by acid leaching.

There are numerous other instances in mineralogy, pyrometallurgy, cement, ceramic, and glass technology which can be used to convey the importance of having a sound theoretical outlook on phase equilibria.

It is clear that students will profit if means can be provided for simple and attractive demonstrations which give a direct insight into the processes of chemical change occurring at high temperatures, and from which simple phase diagrams can be constructed. It is the purpose of this communication to describe a simple and elegant technique which achieves this objective.

Traditional experimental methods of establishing phase diagrams have fallen into two main categories. For mobile systems, e.g., simple salts, dynamic methods of thermal analysis are used. Cooling curves are plotted and temperature arrests accompanying phase changes are sought. This approach has found extensive application particularly in metallic systems; a very comprehensive account of the method has been given by Hume-Rothery, Christian, and Pearson (*1*).

For condensed systems, where changes are sluggish, e.g., phosphates, borates, and silicates, confidence has to be placed in freezing the high temperature states by rapid quenching, once the high temperature equilibrium

[1] On temporary transfer from National Chemical Laboratory, D.S.I.R., England.

is assumed to have been attained; the product is then examined by X-ray or optical methods. Both methods supply only indirect evidence and, with the exception of the plotting of simple cooling curves, do not lend themselves readily to student studies. Most experimental difficulties have been overcome by recent developments in hot stage microscopy, which is rapidly becoming established as an important tool in research laboratories. There have been many hot stage microscopes described but these have found limited use in both research and teaching through being either too expensive, too elaborate, or of restricted application. With the recent improvements here described, however, small quantities of materials can be held under continuous observation while the temperature can be rapidly manipulated and accurately measured up to 1750°C. In addition, the cooling or heating curves of the microscopic specimens can be recorded, which permits phase reactions to be related to an accurately known thermal history.

Developed from an original idea by Ordway (*2*), the basis of the technique is the use of a thermocouple microfurnace which registers its own temperature. Compared to the refinements introduced later by Welch (*3*, *5*), the earlier circuitry of Ordway was complicated and expensive.

The samples (200–500 μg) are held within a small U loop at the junction of the thermocouple, which serves as both the heater and the thermometer. Welch overcame the electrical problem of isolating the applied voltage, which supplies the heating current, from the thermoelectric emf by the use of silicon diodes. These pass only the positive half-cycles of the applied voltage to heat the couple while a phased switch (a synchronous convertor or "chopper") allows the thermoelectric emf to be measured during part of the intermediate half-cycles. The block diagram, Figure 1, illustrates this arrangement. The thermocouple is mounted in a draft-proof cell, Figure 2, on the stage of a microscope through which all crystallo-chemical changes within the system can be observed. In this simplest form the apparatus is very inexpensive and simple to make. Further adaptations to this basic circuit were made by Mercer and Miller (*6*) who introduced two-channel heating and incorporated an oscilloscope or high speed chart recorder which records directly the cooling curves of the specimens held in the thermocouple loop.

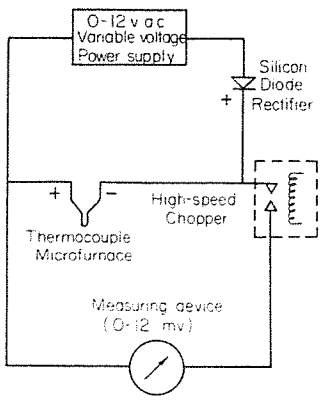

Figure 1. Block diagram of microfurnace power supply and measuring circuit.

Although the literature adequately describes these developments and gives details of construction, a complete list of components and explanatory diagrams for assembly of the apparatus are reproduced in this paper.

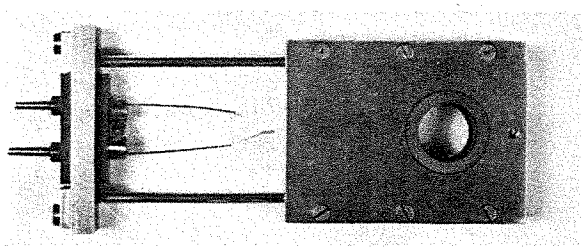

Figure 2. Thermocouple and draft-proof cell.

Components

Double-pole, double-throw switch, 10 amp 220 v.
Toggle switch, 10 amp 220 v.
Dual track autotransformer 0–230v (Zenith Type V5H–2B). A single track autotransformer is sufficient for equilibrium studies.
2 Silicon rectifiers P.I.V. 200 v, average rectified forward current, 3 amp (Texas Insts. Ltd., Type 1S 401).
Synchronous converter. On time, $^1/_3$ of cycle. (G. Kent Ltd., Type NEZ 7501, setting A.)
Resistor 4 KΩ 20 w.
Condensor 0.25 μf.
2 Condensors 3000 μf.
Step-down transformer 220–12 v, 5 amp.
2 Resistors 10Ω $^1/_2$ w.
Potentiometer 0–12 mv (Leeds and Northrup Student Potentiometer).

Polarizing microscope (× 100 magnification). An ordinary microscope with pieces of "Polaroid" material in the filter holder and the draw tube is quite adequate.

Thermocouple wire
0.2 mm 5% Rh–95% Pt
0.2 mm 20% Rh–80% Pt
0.5 mm 5% Rh–95% Pt
0.5 mm 20% Rh–80% Pt

Oscilloscope or high-speed chart recorder.

The oscilloscope must have a high dc sensitivity (100–200 μv/cm) and the time base should include a sweep rate of about 1 sec/cm. The recorder should have a pen sweep time of not greater than 0.5 sec for a full-scale deflection, a chart speed of 1 in./sec, and the full-scale sensitivity should preferably be adjustable between 0–1 mv and 0–10 mv. These requirements, for recording cooling curves, can be regarded as a luxury for many teaching purposes. The cost of the parts, exclusive of equipment usually available in a teaching laboratory, is less than $70.

Notes on Construction and Operating Instructions

The wiring, Figure 3, is simple. It is recommended that the direction of the heating current be arranged such that the Peltier effect at the thermojunction produces localized cooling. This is achieved by connecting the rectifier output to the 5% Rh leg of the thermocouple as shown in the circuit diagram.

Choice was made of the 5–20% Rh/Pt couples because of their very low thermoelectric emf output up to 100°C; this enables any cold-junction error to be

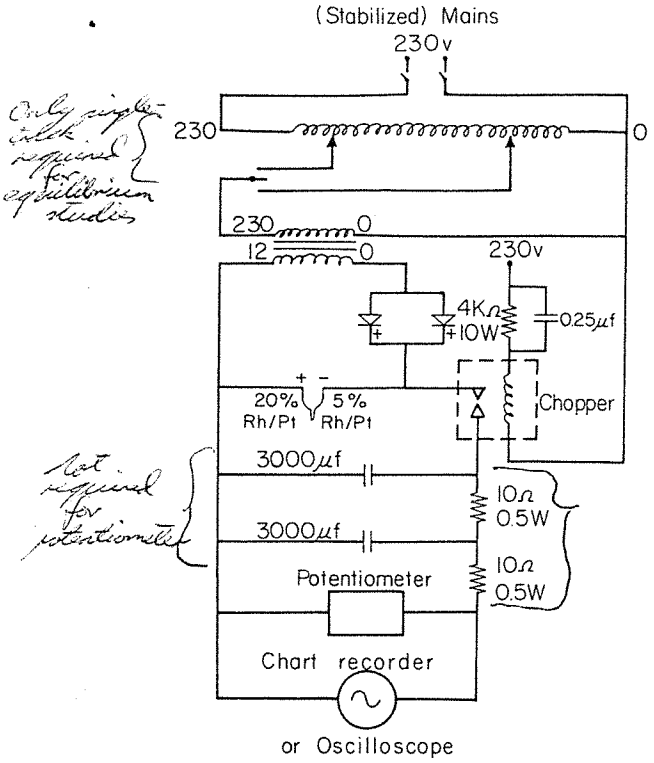

Figure 3. Circuit diagram for thermocouple microfurnace.

neglected. In fabricating the thermocouples, approximately 1 in. of the 0.5 mm wire is spot-welded or impact-welded to about $^3/_4$ in. of the corresponding 0.2 mm wire. A neat butt-weld between the two 0.2 mm wires can be made with practice, using an oxy-gas microflame. An uneven weld should be avoided in order to prevent thermal gradients at the junction.

The U-shaped loop is made at the thermojunction, as shown in Figure 4, by pinching the wires over a metal foil of suitable thickness. To ensure thermal symmetry of the specimen the limbs of the couple near the junction should be kept parallel and should not be separated by more than 0.2 mm. The 0.5 mm wire may be reclaimed from damaged thermocouples but the 0.2 mm wire must be regarded as expendable.

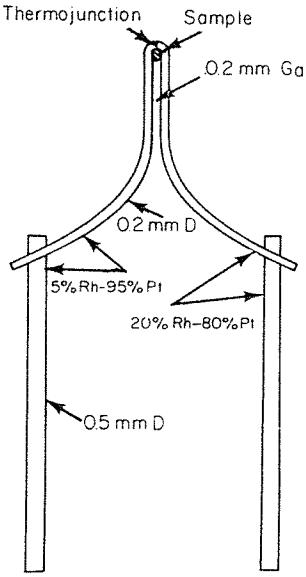

Figure 4. Construction of the thermocouple.

Reference should be made to Welch's original paper (*3*) for details of construction of the draft-proof cell. Alternatively, a cell can be purchased, since a sophisticated model of this hot stage microscope and its accessories is commercially available.[2] In its essentials, the cell, Figure 2, is a hollow metal block with windows through which the thermocouple tip can be viewed. The thermocouple is mounted on a base plate in two separate brass sleeves connected by pins to a matching plug which connects it to the power supply. The base plate is made to be a push-tight fit into the cell which is suitably pegged onto the stage of the microscope. To prevent sagging of the thermocouple the microscope is operated with the stage vertical.

The magnification requirements of the microscope are modest (×100), but where anisotropic crystals are concerned the visual effects are more rewarding when polarized light is used (*4*).

Specimens can be mounted either by melting them onto the thermocouple at the thermojunction, or by transferring small quantities of an aqueous or acetone slurry. Care should be exercised to keep the temperature during mounting to a minimum in order to prevent volatilization; this represents the greatest experimental hazard of the technique because of the high area: mass ratio of the microdroplets.

When mixtures are being examined, it has been shown that reproducible results between different samples of the same batch are obtained by fine grinding followed by mechanical mixing in a Wig-L-Bug grinder. Another procedure to be recommended is bulk melting of the mixes followed by grinding. Care must again be taken to reduce volatilization to a minimum.

Student Applications

(a) Melting Point Determinations

The melting behavior of compounds which fuse between the temperatures of 100°C and 1750°C can be rapidly explored. Although the accuracy of measurements below 300°C is limited due to the low thermoelectric output in this range, melting points above 100°C can be obtained to within ±5°C providing a potentiometer with a discrimination of 0.01 mv is available. In the higher temperature regions, reproducibility to within ±3°C can be obtained.

(b) Determination of Solid State Transitions

Polymorphic changes of anisotropic compounds are often accompanied by striking color changes under crossed polarizers. This change in birefringence is particularly spectacular in the case of the alkali metal sulfates; the transformation temperatures observed under the hot stage microscope agree with published values. If the facility for thermal analysis is available, the heat effects accompanying the changes can be displayed on the oscilloscope or high speed chart recorder. Figure 5 shows the cooling curve between 830°C and ambient temperature of lithium sulfate, with the arrest clearly shown at the known inversion temperature.

This series of observations can form the basis for a

[2] Griffin and George Ltd., Alperton, Wembley, Middlesex, England.

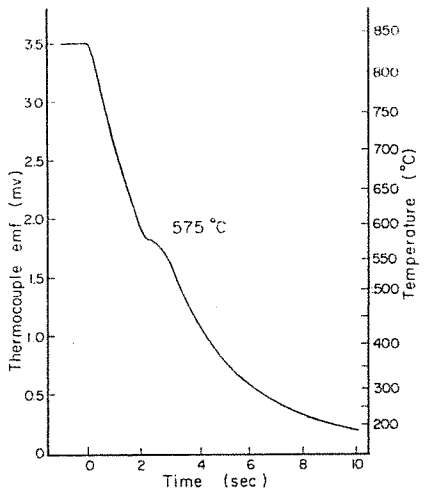

Figure 5. Cooling curve for Li_2SO_4 between 830°C and room temperature.

discussion of the crystal chemistry of the AB_2O_4 compounds, with particular reference to the influence of cation effects (7).

(c) Plotting of Simple Phase Diagrams

This is the most valuable application for teaching purposes. Students in this University have within 5-hour practical periods successfully plotted simple binary phase diagrams, examples of which are reproduced in Figures 6, 7, and 9. Within this time the following operations are completed:

(i) Weighing, grinding, and mixing the components. Approximately a dozen mixes are made differing by increments of roughly 8–10 mole %. If these samples are prepared for the students, the determination can be performed in 3 hours.

(ii) Melting a small quantity of sample into the clean thermocouple loop.

(iii) Determination of the liquidus, solidus, eutectic, and any other observable reaction temperatures. The liquidus temperature is that at which the smallest observable crystal remains in equilibrium with the melt while the solidus temperature is that at which the last drops of liquid solidify on cooling. Alternatively, the solidus may be judged as the temperature at the onset of collapse of the solid. Constancy of the solidus over an extensive range of compositions establishes eutectic behavior.

(iv) Cleansing the thermocouple by repeated heating and dipping into hydrochloric acid, reloading with a duplicate sample and repeating the observations.

(v) Plotting the phase diagram.

Of the three diagrams shown, the simplest is that of the Na_2SO_4–NaCl binary, Figure 6, which exhibits simple eutectic behavior. The thermodynamics of cryoscopy can also be illustrated with some effect from this phase diagram. The attention of students can be drawn to a use of phase diagrams, frequently made by metallurgists, whereby approximate latent heats of fusion of the end member components are calculated by application of the Clausius–Clapeyron equation in the form:

$$\frac{d \ln N_1}{dT} = \frac{\Delta H_f}{RT^2}$$

where:

N_1 = mole fraction of solvent in the solution
ΔH_f = molar latent heat of fusion of the solvent
R = gas constant per mole
T = liquidus temperature at composition N_1

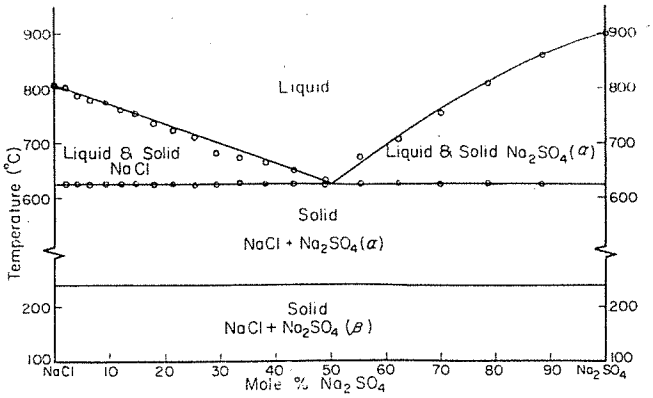

Figure 6. Phase diagram of the binary system NaCl–Na_2SO_4.

With the aid of this equation and Figure 6, the latent heats of fusion of Na_2SO_4 and NaCl were calculated to be 5.2 Kcal/mole and 6.8 Kcal/mole, respectively; these values were computed using the most linear portions of the liquidus profiles. The results may be compared with the values quoted in the literature, 5.75 ± 0.1 Kcal/mole and 6.9 ± 0.4 Kcal/mole, respectively (8). Any discrepancies originate from experimental errors in determining the slope of the liquidus profile and in deviations from ideality.

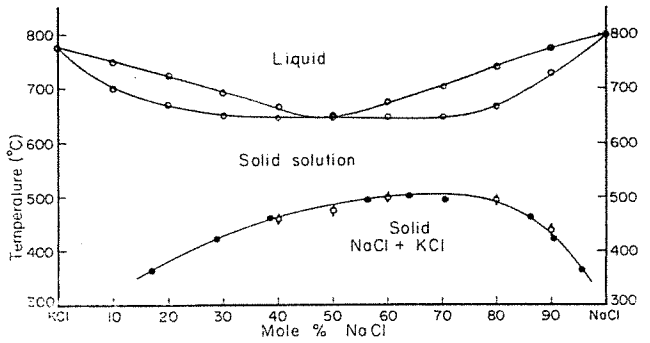

Figure 7. Phase diagram of the binary system KCl–NaCl (O, present work; ● Barrett and Wallace, ref. (9).

The KCl–NaCl system, Figure 7, not unexpectedly, shows that solid solution occurs between the end members. A microscopic thermal analysis at one composition point in this system is shown in F gure 8: the agreement between the reaction temperatures displayed on a family of such curves and those determined visually at corresponding compositions is excellent.

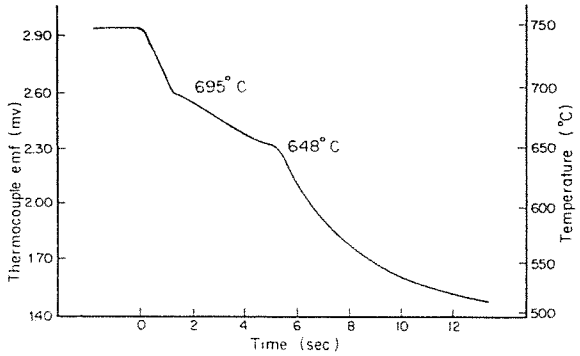

Figure 8. Cooling curve for 30 mole % NaCl–70 mole % KCl mixture.

In addition, ex-solid solution phenomena are manifested by well-defined cracking of the specimens; the grain boundaries can be reannealed a few degrees above the ex-solution temperatures to reproduce homogeneous solid solution. These temperatures of unmixing agree well with those of Barrett and Wallace (*9*), as indicated on Figure 7.

Where solid solution occurs latent heats of fusion may also be determined by using the modified relation:

$$\frac{d \ln (N_1'/N_1)}{d T} = - \frac{\Delta H_f}{RT^2}$$

where:

N_1' = mole fraction of solvent in the solid solution
N_1 = mole fraction of solvent in the liquid solution in equilibrium with the solid solution at temperature T

The latent heats obtained in this fashion may be expected to exhibit large discrepancies from the results of more accurate determinations because of the considerable departures from ideality.

In the carbonate system (Figure 9), students should only concern themselves with the liquidus behavior as there are difficulties and complications, some of which have only recently been resolved (*10*), in the solidus and subsolidus regions.

Although an earlier investigation by Eitel and Skaliks (*11*) indicated compound formation, by a very small peak in the liquidus at the equimolar composition, this has not been detected in the present investigation.

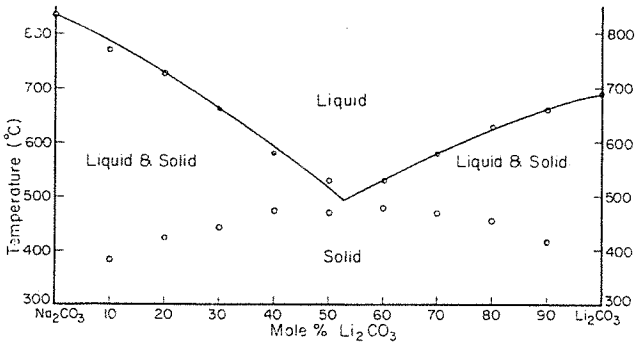

Figure 9. Phase diagram of the binary system Na_2CO_3–Li_2CO_3.

Potential Applications

The compilations "Phase Diagrams for Ceramists" (*12*), "Solubilities of Inorganic and Organic Compounds" (*13*), and "International Critical Tables" (*14*), provide a rich source of further exercises; a wide choice of systems of varying complexity is available for selection according to the discretion of the supervisor. A recent publication (*15*) on the ternary system Cs_2SO_4–K_2SO_4–Li_2SO_4 should provide an uncomplicated but colorful introduction to the plotting of ternary diagrams.

It may be of value to consult the research papers *16–21)* published on the application of the technique to problems in mineral and complex oxide chemistry. These should make clearer the full scope and potential of the arrangement and may well be suggestive of more ambitious practical exercises, particularly in the mineralogical field, since a comprehensive high temperature reconnaissance of the behavior of rocks or nonopaque minerals can be rapidly made.

For advanced students this hot stage microscope can also provide a stimulating introduction to X-ray powder photography. The specimens from the thermocouples, crushed with care in a small agate mortar, provide sufficient sample to load into a very fine capillary which can then be mounted in a Debye-Scherrer camera. Considerable satisfaction should be experienced in identifying a compound whose growth has been completely controlled and continuously observed.

Although the most effective working range of the 5–20% Rh/Pt thermocouples is at high temperatures, the interests of the organic chemist are not excluded as it has been found that measurements of temperature to within ±5°C can be made over the range 100–300°C. Alternatively, the use of more suitable thermocouples, e.g., copper–constantan, can be explored. This allows consideration to be given to many of the techniques suggested by McCrone (*22*).

A film entitled "The Building Research Station Hot Stage Microscope" is available on loan on application to the Building Research Station, D.S.I.R., Garston, near Watford, England, while copies of our "Instructions to Students" may be obtained by application to L. Glasser.

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