Experiment 6.

Phase Studies by Hot-Stage Microscopy.

Summary:

Many methods are available for phase studies. This experiment illustrates one of the more elegant methods for phase studies involving solids, where a platinum-rhodium thermocouple is used both as heater and for temperature measurement, while phase changes of the heated material (total weight, about 200 µg.) are observed microscopically under polarized illumination.

References:

"Fusion Methods in Chemical Microscopy" by W.C. McCrone, Jr., Interscience Pub., New York. 1957.

"Crystals and the Polarising Microscope" 3rd edition, by N. Hartshorne and A. Stuart. Arnold, London.

"Thermal Analysis by High-Temperature Microscopy" by R.A. Mercer and R.P. Miller, J. Sci. Instr. (1963) 40, 352 and references therein.

Discussion:

Of the many methods available for phase studies, some are appropriate for one set of components, others for another set. Even when a number of methods is suitable for a given system it is not necessarily true that one method should be used to the exclusion of all others, for the methods are complementary, often giving more than simply the temperature of a phase change. For instance, differential thermal analysis gives a measure of the heat change in a phase reaction, thermogravimetric analysis measures the weight change, dilatometry measures volume changes, etc. Microscopic examination of a system undergoing a solid transition or melting is also useful, for the conditions of crystallization, the nature of the solid polymorphs, etc., can be observed. This is even more significant when a polarising microscope is used, for changes in the solid phases can easily be observed from changes in birefringence. Birefringence occurs in an anisotropic crystal because the refractive index for light varies with direction in the crystal. In such a crystal, polarized light is turned from its plane of polarisation and the crystal appears coloured between crossed polars, the colour depending on the thickness of the crystal and the values of its refractive indices.

An additional factor in favour of the microscopic method of phase determination is its very great rapidity. A conventional hot-stage microscope will permit the complete determination of a binary eutectic diagram in 2 – 4 hours; the present technique is even faster, for both heater and sample have negligible heat capacity compared to the rate of heat input, and there is no waiting-period for cooling or heating.

Equipment:

The apparatus consists of a thermocouple contained in a jacket having windows to permit optical examination. The thermocouple is heated for half of each cycle, a rectifier stopping the flow of current in the other half-cycle. For this period of time, a synchronous convertor ("chopper") is switched on and permits temperature measurement by means of the potentiometer. The switching is so fast that, coupled with the condensor in the circuit, it is not noticeable during the measurement, while the heat capacity of the system is sufficiently large to prevent temperature fluctuation during the small "off" time of the heater.

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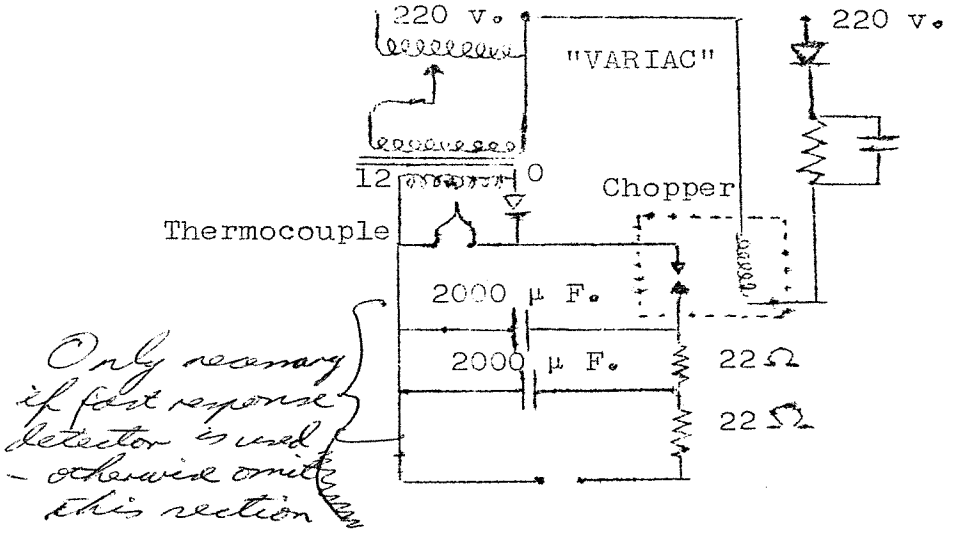
The circuit is as follows:



Caution: Avoid over-heating of the thermocouple which will reduce its life considerably.

Method:

Suitable mixtures of the components will already be prepared or otherwise must be prepared as follows. Weigh the mixture into a porcelain crucible (about a gram must be used to obtain a homogeneous mixture, although very much less will be used in the actual determination) and melt it with the lid on the crucible to reduce evaporation. The mixture should not be retained at high temperatures for longer than necessary as differential evaporation might otherwise alter the composition of the mixture. When thoroughly mixed, allow the melt to cool and grind the solid in a mortar and pestle. Repeat this for all the mixtures required.

Clean the thermocouple with water or suitable reagent, and, if necessary, pull it into shape by pulling it over the edge of a piece of copper foil of about the thickness of the thermocouple wire. Connect it into the heater circuit and, with the "Variac" turned up to a suitable value, transfer a tiny bead of the mixture from some powder on a spatula to the thermocouple. This bead should just fill the loop in the thermocouple, its diameter being about that of the thermocouple wire. Turn the "Variac" down to zero.

Push the holder into its jacket, with cover-slips held over the opposite holes in the jacket by means of plasticine or magnetic rings. Screw the assembly to the microscope stage. The microscope stage must be in the vertical position, with the jacket arranged so that the thermocouple assembly can easily be removed. Adjust the position of the assembly so that the bead is in view. Adjust the eyepiece extension tube so that the polars are crossed.

Raise the temperature of the thermocouple slowly by adjusting the "Variac" and read the temperature of any transitions by means of the potentiometer and thermocouple table supplied. The temperature to be noted is that at which the transition occurs just at the thermocouple junction; temperature gradients are very considerable and transitions observed elsewhere will not lead to reliable temperatures. Note carefully the changes occurring at each transition. If it is difficult to set the "Variac" exactly to the transition temperature, estimate it by straddling it a few times.

When a sample has been completely examined, remove the

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Experiment 6 Continued:

thermocouple assembly from its jacket and dip the heated thermocouple into water to dissolve away the sample. Melt some of the next sample onto the thermocouple and dissolve it away, and then melt a final bead of this sample onto the thermocouple. This process should remove any of the first sample still attached to the thermocouple; cleanliness is essential here for small contaminations could cause considerable changes in the compositions of the small samples.

Report Card:

Report system, nature of phase diagram and significant temperatures with the corresponding compositions.

Apparatus:

Microscope with polarizer and analyser.
Hot-stage jacket, thermocouple holder and thermocouple.
Heater control.
Potentiometer and galvanometer.
Mortar and pestle.
Small spatula.
Wash bottle.
5 x Porcelain crucibles with lids.
5 x pipe-clay triangles.
2 x bunsen burners.
5 x tripod stands.
10 x sample bottles.
50 ml. beaker.
Dissecting Needle.
1 inch square of copper foil.

Reagents:

One mixture of the following:

KCl and NaCl.

LiCl and KCl.

Other mixtures, to be decided.

CONTINUED:

ADDENDUM.

In order to increase the versatility of the apparatus, a second auto-transformer has been added to the circuit, in parallel with the first; a change-over switch selects which of the two auto-transformers is in circuit. Together with a high-speed chart recorder, this modification enables cooling curves over hundreds of degrees to be recorded in a few seconds.

The first auto-transformer is adjusted to raise the thermocouple and sample temperature to just above the transition to be examined; the second auto-transformer is then switched in and adjusted to set the sample temperature some convenient way below the transition temperature -- the greater the difference between the temperature settings of the two auto-transformers, the greater will be the rate of cooling obtained in the subsequent determination of the cooling curve. The Ayrton shunt to the recorder is adjusted so that the higher temperature gives a nearly full-scale deflection.

With the first auto-transformer in circuit, the recorder chart-drive is switched on and the change-over switch is operated. The thermocouple and sample immediately start cooling to the lower set temperature, and the temperature versus time curve is plotted on the recorder. Rate-of-heating curves may be recorded in a similar fashion. Because of the small heat-capacity of the system, cooling is very rapid. In addition, temperature arrests are shown up rather well because the enthalpy of the transition is required to heat up very little material other than the sample itself, in contrast with usual procedures where the sample container has a very significant heat capacity. The temperature arrests may be shown up even more vividly by loading the thermocouple with more sample than usual. However, this probably leads to a lower accuracy because of the considerable temperature-gradients within a large sample.

Occasionally, on operating the change-over switch, a sharp initial deflection of the recorder may occur. This is due to the switching occurring during a peak of the heating cycle, and should be ignored.

Comments:

For plotting equilibrium phase diagrams the procedure described under "Method" is more satisfactory, since it is a strictly equilibrium technique. However, transitions which are affected by the rapidity of cooling can be most easily examined in the second way.

Thus, glass formation depends on a cooling too rapid for crystallization to occur. Since the second method is best adapted to rapid cooling, this has been used to study glass formation. Rates of cooling of up to 20,000 deg C $sec.^{-1}$ have been obtained by squirting the sample with a liquid at the moment of switching to a lower temperature.

Calculations:

Using the Clausius-Clapeyron equation

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

where N_1 = mole fraction of solvent in the solution, approximate latent heats of fusion of the components in a simple eutectic

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system can be calculated.

Similarly, where solid solution occurs latent heats of fusion may be determined with the modified relation:

$$\frac{d \ln (N_1'/N_1)}{dT} = -\frac{\Delta H_f}{RT^2}$$

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.

Report Card:

In addition, report latent heats of fusion of components in phase system studied.

Additional References:

"Metallurgical Equilibrium Diagrams" by W. Hume-Rothery, J.W. Christian and W.B. Pearson, Inst. of Physics, London 1952.

"A Versatile Hot Stage Microscope" by L. Glasser and R.P. Miller. J. Chem. Educ. (1965) 42, 91.