Other Techniques

Thermogravimetry

Thermogravimetry (TG) is a technique by which the weight of a substance, in an environment heated or a cooled controlled rate is recorded as a function of time or temperature. Derivative thermogravimetry exploits the first derivative of the TG curve.

Thermogravimetry seems to have been used first in 1912 in the study of the efflorescence of hydrated salts and has since been an aid in the quantitative investigation of decomposition reactions; it is at its best when used in conjunction with calorimetric analysis.

The equipment consists of a precision balance, a furnace with a programming facility, a reaction chamber and a suitable recording system. The assembly has to be capable of continuously registering any weight changes in the test sample whilst the latter is being heat–treated. There are essentially two types of apparatus – the null–point balance and the deflection balance. In the former, any movement of the balance beam caused by weight changes is counteracted by a restoring force to bring the beam back to its original position; this force is then taken to be proportional to the weight change concerned. Such instruments are readily adaptable to operation in a vacuum. The deflection instrument can be more robust and reliable because it is based a conventional analytical balance.

The thermocouple is usually placed in direct contact with the sample. However, any connections to the support must afford an extremely small torque, or in the case of null balance instruments, a small or highly reproducible torque. TG is a quantitative and dynamic technique, and a number of factors can effect the shape of the TG curve. Temperature gradients, air buoyancy, convection currents within the furnace tube and other factors contribute to the so called *buoyancy effect*† in which the weight of an inert, empty crucible changes with temperature. A correction curve can be determined to compensate for this effect, making certain that the conditions of such a calibration correspond to those of the actual experiment.

TG gives absolute changes in sample weight so that the calculated extent of reaction is not affected by the heating rate used, although the start and finish temperatures are a function of heating rate because of kinetic barriers.

The main applications of TG include the measurement of thermal stability, ageing characteristics, decomposition, reactivity and the structures of compounds. It has obvious uses in the determination of the moisture content of powders, water of hydration and of carbon monoxide and carbon dioxide evolution from carbonates etc. Decomposition reactions can be studied in a variety of imposed environments to yield information on the reduction of metal ores. In organic chemistry the technique has been widely used to study the degradation of polymers and to investigate the pyrolysis of coals, peats and bitumens. TG can also be used to record isothermal and isobaric weight changes.

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† When a specimen is heated in ambient air or any gas of comparable density, the apparent weight changes with temperature due to the change in weight of the displaced gas; the specimen then appears to gain weight on heating.

Evolved Gas Analysis

Useful information can often be gained by studying the gases which arise through the thermal decomposition of compounds. Evolved Gas Analysis (EGA) apparatus can be of two kinds:

a) That in which the gas is evolved inside the gas detector or analysing apparatus, enabling the detection of transient species evolved during the course of the decomposition reaction. Difficulties can arise in the control of the temperature, pressure and degree of dilution of the sample environment.

b) That in which the evolved gas is led into a separate detection system, enabling more flexible apparatus design, the possibility of pretreating the gas before analysis, and generally better control of the specimen environment. The possibility of secondary reactions occurring during the passage of the gases from the source to the detector cannot be discounted.

Many types of detectors have been used for evolved gas analysis; those which sense the thermal conductivity of gasses are popular, but not very discriminating; gas–density and ionisation detectors are also used. Gases can be absorbed in suitable solvents for subsequent chemical analysis, and the use of mass spectrometers for high–resolution analysis is common.

References to Thermal Analysis Techniques

Books and Reviews

1 M. I. Pope and M.J. Judd: ‘Differential Thermal Analysis’, London, Heyden, 1977. Analysis’, 1,2, London, Academic Press.

2 J. Sestak, V. Satava and W.W. Wendlandt: Thermochimica Acta, 7, 333 (1973).

3 A. L. Greer: Ph.D. Thesis, University of Cambridge (1979).

4 V. Konryushin and L.N. Larikov: J. Mat. Sci., 13, 1 (1978).

Specific References

5 A. L. Greer: Thermochimica Acta, 42, 193 (1980). Curie point measurement in the DuPont DSC system.

6 R. A. Baxter:‘Thermal Analysis’, 1, 65 (1969) - eds. R.F. Sswenker and P.D. Garn, New York, Academic Press. This is the original paper on the Dupont DSC system.

7 H. K. Yuen, C.J. Yosel: Thermochimica Acta, 33, 281 (1979). Specific heat measurement in the DuPont DSC system.

8 L. M. Clareborough, M. E. Hargreaves, D. Mitchell and G. West: Proc. Roy. Soc., A215, 507 (1952). Description of the original DSC concept, and measurement of the stored energy of deformation.

9 M. G. Scott and P. Ramachandrarao: Mat. Sci. & Eng. 29, 137 (1977). Deals with the establishment of the baseline and some kinetic investigations.

10 M. G. Scott: J. Mat. Sci., 13, 291 (1978). Kinetics of glass crystallisation. Anal. Chem., 29, 1702 (1957). Deals with the Kinetics of non-isothermal, homogeneous transformations.

11 D. W. Henderson: J. Non-Cryst. Sol., 30 301 (1979). Kinetics of non-isothermal, nucleation and growth transformations.

12 E. A. Marseglia: J. Non-Cryst. Sol., 4, 31 (1980). Kinetics of non-isothermal nucleation and growth transformations.

13 J. W. Christian: 'Theory of Transformations in Metals and Alloys'. 2nd ed., (1975), Part 1, Pergamon Press, Oxford. Elegant and comprehensive review on the formal theory of transformation kinetics.

14 K. Matusita and S. Sakha: Non-Cryst. Sol., 38-39, 741 (1980). Kinetics of glass crystallisation.

15 A. P. Gray: Thermochimica Acta, 1, 563 (1970). Polymer crystallisation.

16 R. O. Simmons and R.W. Balluffi: Phys. Rev., 117, 52 (1960) & 125, 862 (1962). Dilatometric measurement of vacancy concentrations.

17 M. Perakh: Surface Technology, 4, 527 (1976) & 4, 538 (1976). Dilatometric determination of stress.

18 T. Inoue and B. Raniecki: J. Mech. Phys. Sol., 26, 187 (1978). Use of dilatometry in the prediction of thermal hardening and transformation stresses.

19 J. J. Stobo and B. Pawelski: J. Nuc. Mat., 4, 109 (1961). The influence of texture on the anisotropy of thermal expansion.

20 J. Valentich: J. Mat. Sci., 14, 371 (1979). General dilatometry.

21 W. G. Hall and T.N. Baker: 'Phase Transformations', York Conference, (1979), No. 11, Series 3, 2, 11-90. Resistively changes during the ageing of steels.

22 J. Bass: Advances in Physics, 21, 431 (1972). Resistance measurements and the deviations from Mathiesson's rule.