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THERMAL ANALYSIS IN REACTIVE ATMOSPHERES

Its practice and applications in high temperature technology

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By using reactive atmospheres, the area of application of thermal analysis is expanded considerably to cover many aspects of high temperature research into fuels, extractive metallurgy, materials and catalysts. This article reviews the design of apparatus and its application in kinetic and thermodynamic studies involving atmospheres such as H_2, CO, N_2, NH_3, CO_2, H_2O, $SO_{2\,\mathrm{or}\,3}$, H_2S, S_2, Cl_2, HCl, F_2 and HF at low or high pressures and as low pressure plasmas. Apart from gas-solid reactions, the important influence of a controlled product gas atmosphere on decomposition reactions is discussed also. Gas-solid adsorption and solubility studies are not included.

Thermal analysis is usually conducted in atmospheres which do not react chemically with the sample, using apparatus optimised for noncorrosive gases. The most commonly used reactive gas is O_2 (or air) at ambient pressure for monitoring oxidative stability and for quantifying carbonaceous material by combustion. However, as Table 1 shows, thermal analysis has been applied in a great variety of reactive atmospheres – gases, vapours, plasmas, at pressures from micro to kilo bars – largely to research and development problems in high temperature technologies. These technologies utilize gas-solid and decomposition reactions and require kinetic and thermodynamic measurements.

This review describes first the apparatus needed for work in special atmospheres, then the measurement of thermodynamic functions for technologically important gas-solid systems. Next the important effects of a controlled product gas atmosphere on the mechanism of a decomposition reaction are outlined. This leads to a section on kinetic studies of gas-solid and decomposition reactions under the headings of specific atmospheres.

Some remarks made below are also relevant to thermal analysis in self-generated atmospheres, a subject reviewed elsewhere [1].

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Table 1 Areas of application of thermal analysis using reactive atmospheres

ATMOSPHERE	APPLICATIONS
O_2	Combustion, extractive metallurgy, oxidation stability tests, carbon analysis.
H_2, CO	Extractive metallurgy, coal hidrogenation, catalysts, materials science, hydrogen storage.
N_2, NH_3, NO_2	Nitriding using N_2 or NH_3, decomposition of catalysts, and propellants in NH_3, extractive metallurgy using NO_2.
CO_2	Exploitation and analysis of carbonate minerals, processing fuel gases, corrosion.
H_2O	Coal gasification, materials science, reversible dehydration reaction analysis of plaster.
$SO_{2 \text{ or } 3}$	Cleaning combustion gases, extractive metallurgy.
H_2S	Cleaning fuel gases, corrosion.
Cl_2, HCl etc	Extractive metallurgy, analysis of ceramics.
F_2, HF etc	Nuclear fuel processing.
Plasmas	Materials science

Experimental

Apparatus

Thermal analysis has been performed in gases and vapours at low and high pressures and in low pressure plasmas. Plasmas and vapours pose specific problems discussed below, but otherwise the apparatus design is dictated by the corrosive nature of the atmosphere, its pressure and its flow arrangement. A flowing atmosphere is preferred at normal and high pressures to facilitate mass transfer but at low pressures the atmosphere is usually static. Below, corrosion problems are discussed for furnaces, thermocouples and thermobalances, and the difficulties in generating and using controlled atmospheres are considered separately for gases, vapours and plasmas.

1. Corrosion Problem

(a) *Furnaces*

The most corrosive conditions are in the hot zone of the furnace but a suitable ceramic can usually be found (e.g. alumina or mullite). Silica glass is attacked by H_2O and H_2 near 1000°. Nickel furnace tubes and thermocouple protection sheaths were used by Mitkin *et al.* [2] in TG and DTA apparatus for studying the reactions of solids with F_2 and HF [3–5] at temperatures up to 600°. In high pressure apparatus, a small furnace may be enclosed by a cold pressure vessel [6, 7], or the furnace may surround the pressure vessel [8, 9]. In the latter case, the pressure vessel (usually a tube) is of a suitable alloy; for example, Li and Rogan [10] use Inconel 617 with an alumide coating for work at 1100° and 60 bar of an atmosphere containing H_2 and H_2S.

In one apparatus [11] for TG in high pressure corrosive gases, the sample holder hangs inside a graphite susceptor which is heated inductively by a cold coil, so minimizing hot corrosion.

DTA or DSC can be performed using a sample holder which is in effect a mini reactor with its own inlet and outlet tubes for a flow of reactive gas at high or normal pressure. This approach is exploited by Setaram in their DSC 111 and C80 calorimeter, which are in a class of their own for versatility in controlled atmosphere work [12].

(b) *Thermocouples*

The choice of alloys for exposed thermocouple wires or protection sheaths depends on the atmosphere, its pressure and temperature. Precious metal thermocouples like Pt13%Rh-Pt are suitable for most atmospheres but embrittle in H_2 above 700° and at even lower temperatures in high pressure H_2. However, chromel-alumel thermocouples have been used for DTA [7] under 600 bar H_2 at 1000° with no reported complications. Chlorine severely attacks all base metal alloys but corrodes Pt13%Rh-Pt more slowly. The combined TG+DTA apparatus of Gimzewski [13] for operation in chlorine and other corrosive atmospheres employs 1 mm id silica sheaths to protect the thermocouples. Ishii [14] uses the same principle in his DTA apparatus for chlorine atmospheres.

(c) *Thermobalance protection*

Three approaches to TG in a flowing corrosive gas are shown in Fig. 1 (the additional complications for vapours and plasmas are discussed in the section on atmosphere control). In the simplest apparatus, (a), the corrosive gas flows over a quartz spring balance [15] which may be read automatically or by a cathetometer. At the other extreme is the ingenious Sartorius magnetic suspension balance [16], (b). Here there is a magnetic rather than solid connection between the balance in its completely sealed chamber and the sample suspension system (TG or simultaneous TG+DTA) in the furnace tube. Furnace tubes are available for work in very corrosive gases (e.g. Cl_2) and at low or high pressures. The third and most popular approach, (c), is to have a stream of inert gas flowing through the balance chamber and leaving through a narrow tube surrounding the suspension wire. The corrosive gas flows upwards over the sample and leaves via the side tube together with the inert stream. However, if the condensation of vapour product on the suspension wire is a problem, this can be prevented by having the corrosive gas enter the side tube and flow downwards, diluted by the inert gas.

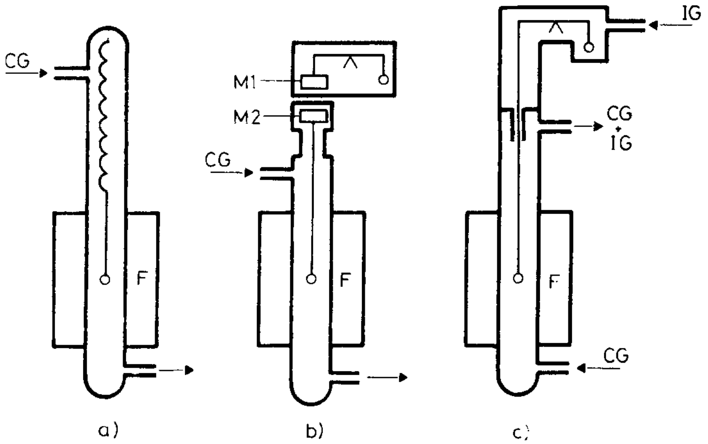

Fig. 1 Three approaches to TG in a flowing corrosive atmosphere: (a) the microbalance is a corrosion-resistant spring; (b) in this Sartorius design, the microbalance is completely isolated in its own chamber and supports the sample suspension rod by attraction between magnets M1 and M2; (c) a chamber containing the microbalance (spring or electronic) is continuously flushed with inert gas.

(Key; *F* = furnace; *CG* = corrosive gas: *IG* = inert gas)

Most commercial TG equipment, whether vertical or horizontal, can be adapted for corrosive gas work at ambient [17–19], and in some cases high pressures [8, 10, 20–22], by using the inert purge principle in Fig. 1(c). For example, the author [13] has used the arrangement in Fig. 1(c) in a combined TG+DTA instrument based on the CI Electronics balance. In Fig. 1, methods (a) and (b) but not (c), are applicable to static low pressures of corrosive gas.

2. *Atmosphere control*

(a) *Gases*

The concentration of the reactive gas can be set by dilution with an inert gas or by controlling the pressure of the undiluted gas. The literature on vacuum microbalance techniques [23–25] contains many examples of pressure control systems, therefore only the dilution method will be discussed.

The concentration of a reactive gas in a diluent is set by mixing metered flows of the gases, with special precautions at high pressures. Low concentrations (down to 10 ppm) can be achieved using, for example, a motor-driven syringe pump but the buffer capacity of such mixtures for gas-solid reactions is low. In such cases, it is sometimes possible to use equilibrated mixture of high buffer capacity, such as H_2O+H_2 or CO_2+CO for low O_2 levels, H_2S+H_2 for low S_2, and $HCl+H_2$ for low Cl_2.

(b) *Vapours*

Problems arise in generating vapours and in preventing their condensation in the apparatus, particularly on the sample suspension rod in TG. Thus it is necessary to maintain all parts of the apparatus above the dew-point of the vapour using, for example, heating tape, small furnaces, jackets of hot water, or by situating all or most of the apparatus in a water bath or fan oven [26–28].

The simplest method of generating a vapour atmosphere is to pass an inert gas (at normal or high pressure) through a thermostatted liquid to achieve the saturated vapour pressure. Another method is to vaporise completely a controlled flow of liquid in, for example, a hot tube packed with metal chips, with a metered stream of diluent inert gas at normal or high pressure. It is also possible to generate the vapour in a flame (e.g. H_2O from H_2+O_2). This is rarely employed, but could be useful for studying the sample in the combustion products of a specific fuel.

All the above methods for generating flowing vapour atmospheres are compatible with the three apparatus designs in Fig. 1 at normal or high pressures.

Danielewski and Mrowec [26] have built apparatus for TG in static low pressures (10^{-3} to 1 bar) of pure sulphur vapour. The vapour pressure is set by a thermostatted bulb of liquid connected to the type of apparatus in Fig. 1(a), with a vacuum system to evacuate it initially.

A very different method of generating a static vapour atmosphere is shown in Fig. 2 where a controlled inert gas pressure sets the vapour pressure and boiling temperature in a reflux system. The liquid is boiled by a heater (not a thermostat), and a condenser section dictates the position of the interface between the pure vapour and the pure inert gas. Two versions of the apparatus employ different devices to prevent condensation on the suspension wire in the condenser zone. For example, in Metrot's [29] TG apparatus for studying carbon (~10 g samples) in sodium vapour (10^{-4} – 0.6 bar), an electric current passed through a looped suspension wire maintains its temperature above the dew-point. On the other hand, in the apparatus of Billing and Balesdent [30] for work in sulphur vapour, the suspension wire is protected by a low pressure purge of inert gas.

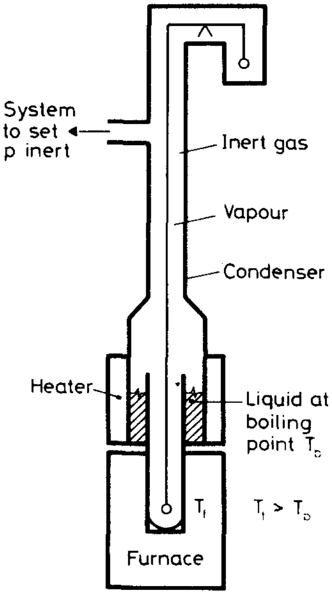

Fig. 2 Thermogravimetry in a refluxing vapour.
A controlled inert gas pressure sets the vapour pressure of the refluxing liquid. The condenser dictates the position of the vapour – inert gas interface. The device for preventing condensation on the suspension rod is not shown (see text).

Setaram and Mettler manufacture accessories for adapting certain of their TG instruments to operate in low pressures of water vapour.

Garn and Kenessy [31] have built an ingenious apparatus for DTA in an undiluted vapour atmosphere (e.g. H_2O or benzene) which can be static or flowing and at any pressure.

(c) *Plasmas*

The numerous peculiar problems associated with generating a stable low pressure DC plasma in a vertical TG system have been overcome by Veprek and Webb [32].The system was sufficiently sensitive to measure erosion rates of graphite of one atomic layer per second at 450°C in a hydrogen plasma. Oswald, Veprek and Wirz [33] have also used TG in low pressure radio frequency plasmas.

Thermodynamic studies

For equilibria of the type

$$AB_{(s)} = A_{(s)} + B_{(g)}$$

TG and DTA can be used to measure the equilibrium dissociation temperature T_d as a function of p_B [34], from which ΔH and ΔS are calculated. The method involves heating $AB_{(s)}$ in an atmosphere with a known value of p_B. When $T_{sample} > T_d$ from the equilibrium p_B v. T curve, the sample begins to decompose. Superheating is needed to overcome kinetic barriers to achieve a measurable ΔT signal from DTA, but with TG much lower heating rates or isothermal steps can be employed to minimize this error. On cooling the decomposition product, $A_{(s)}$, in the same atmosphere, the reverse reaction is detected, with supercooling in DTA experiments. High pressures of $B_{(g)}$ lead to more accurate results as reaction rates are greater at the higher decomposition temperatures.

When a substance is decomposed in a controlled pressure of product atmosphere, the decomposition events in DTA and TG curves are much sharper and almost always occur at a higher temperature than in an inert gas. This behaviour is exploited in the analysis of decomposible substances in a mixture (see section E).

For gas-solid equilibria involving a non-stoichiometric solid, TG can be used at a fixed temperature and reactive gas pressure to determine the equilibrium composition of the non-stoichiometric solid. For example [35], starting with a sample of CeO_{2-x} with known Ce content, the value of x at fixed T and p_{O_2} is determined from the final stable weight. Also, the rate of attainment of equilibrium can be used in some cases to calculate the diffusion coefficient and activation energy for the mobile species in the solid.

Where the equilibrium involves more than one gas (e. g. $MO_{(s)} + H_{2(g)} = M_{(s)} + H_2O_{(g)}$) all pressures must be fixed in an equlibrium study.

Examples of systems studied are given in Table 2.

Table 2 Some thermodynamic studies using thermal analysis with reactive atmospheres

Technique	System	Ref	Atmosphere
TG	CeO_{2-x}	(35)	O_2
	PuO_{2-x}	(36)	O_2
	$BaBiO_{3-x}$	(37)	O_2
	Fe–S	(26)	S_2 (10^{-3}–0.8 bar)
	Cu–S	(30)	S_2 (10^{-3}–1 bar)
	Mg_2Ni–H	(22)	H_2 (1–20 bar)
DTA	$MgSO_4 = MgO+SO_3$	(34)	SO_3
	$Mg(OH)_2 = MgO+H_2O$	(38)	H_2O (1–1000 bar)
	U–N	(39)	N_2
	$LiNi_5$–H	(7)	H_2 (1–200 bar)

The effects of product gas on decomposition mechanisms

Many variables affect decomposition reactions [40] but the focus here is on the chemical effects of a product gas atmosphere.

Many industrial decomposition reactions (e.g. of hydrates, carbonates, sulphates) are reversible; that is, the product gas pressure at the reaction interface is usually high enough to cause a significant reverse reaction [41]. This reverse reaction not only lowers the net decomposition rate, but it can even affect the reaction mechanism [42–46], so influencing the crystallographic nature and microstructure of the product. In that case, atmosphere control becomes a useful new variable for achieving desirable microstructures [47, 48]. However, for the investigator of fundamental chemical kinetics, it is necessary to account accurately for or eliminate the reverse reaction. These points are illustrated very convincingly by Rouquerol and co-workers [42–45], who have exploited the control of product gas pressure, as well as other variables:

(a) to make very reproducible oxide microstructures with close control of surface are, porosity and pore geometry, and

(b) to elucidate reaction mechanisms and establish the conditions under which unambiguous fundamental kinetic measurements can be made.

Examples of this work are given in the following section.

Kinetic studies

Table 1 summarises the areas of application of thermal analysis using reactive atmospheres, and the examples given below illustrate the scope and variety of some of these applications.

1. *Oxigen*

Thermal analysis in O_2 atmospheres is well documented, so only a few topics will be mentioned here.

TG curves are obtained routinely in analytical labs for materials likely to be exposed to air at high temperatures [49], and there have been many fundamental studies [50], especially of metals and alloys. An important recent development is the use of oxygen at high pressures to accelerate long-term oxidation processes. For example [51], the long-term (months) oxidation of lubricating oils can be simulated in about 30 min under 35 bar O_2 at 180° using DSC. TG is widely used to study fossil fuel combustion [52] and sulphide oxidations in extractive metallurgy [53]. In chemical analysis, carbon is determined using TG to follow its complete combustion in O_2.

2. *Hydrogen and carbon monoxide*

(a) In several industrial processes, natural gas is reacted with steam to give H_2 + CO for reducing iron ore to sponge iron. TG studies [54, 55] have helped to optimise the process by clarifying the kinetics of the reduction.

(b) Sohn and co-workers [56, 57] have used TG to study the kinetics and mechanism of the reduction of $CuSO_{4\,(s)}$ by H_2 at 500° as part of a proposed new copper extraction process.

(c) Another proposed route for extracting copper and nickel from suphide ores (MS) uses the reaction $MS_{(s)} + CaO_{(s)} + H_2$ (or CO)$= M_{(s)} + CaS_{(s)} + H_2O_{(g)}$, and TG has been used to screen the reactivity of several suphide minerals [58] and in a kinetic study [59] of pure Cu_2S. Won and Sohn [60] have tried to elucidate the mechanism by a TG study of the $CaO - H_2S$ reaction alone.

(d) TG and DTA have been useful in understanding aspects of coal hydrogenation [61, 126] such as reaction conditions, catalysts and pretreatments. For example, Ghodsi and Neumann-Tilte [8] have built a symmetrical TG apparatus for hydrogenating coal and other carbonaceous substances at temperature up to 1000° and H_2 pressures up to 50 bar. They show the effects of T and p_{H_2} on the rate and extent of reduction of an Italian coal.

Cypres *et al.* [9] from the same institute, have built DTA apparatus to study coal hydrogenation under the same conditions to compliment the TG work. By careful calibration, heats of reaction were quantified for the hydrogenation of a Belgian coal at several pressures.

(e) Thermal analysis studies in H_2 and/or CO are important in understanding the preparation, operation and in estimating the activity of catalysts. For example, Soled *et al.* [62] have used TG to follow the reduction and carbiding of the Fischer-Tropsch catalyst α-Fe_2O_3 in CO, H_2 and CO + H_2 with and without thallium and potassium promoters.

(f) An unusual method of assessing the activity of a catalyst for comparative purposes is to use TG [63] to follow its behaviour during repeated cycles of oxidation and reduction in O_2, He, H_2, He etc.

(g) Thermal analysis in H_2 has been used to identify different forms of a reducible oxide on a support with which it interacts [64] (e.g. NiO on Al_2O_3).

(h) The adoption of hydrogen as a major fuel will require safe and efficient methods of storage, such as the reversible reaction alloy + H_2 = hydride, with alloys like Ln_5Ni, FeTi and Mg_2Ni. TG [22] and DTA [7] in high pressure H_2 have been used to study aspects of these reactions, such as phase diagrams (see section C), heats of reaction, kinetics of hydriding and dehydriding, capacity for H_2 storage, and the effects of repeated cycling.

(i) In materials preparation, various compounds are reduced by H_2 to metal powders or metal-metal oxide composites. For some systems, where there are several intermediate oxidation states, the morphology of the final metal is strongly influenced by the reduction mechanism. For example, by using TG in controlled atmospheres of H_2 + H_2O, it is possible to establish the conditions to produce composites with desired microstructures in the Cu-W-O [65] and Ag-W-O [66] systems much more reproducibly than with H_2 alone.

3. *Nitrogen-containing atmospheres* (N_2, NH_3, NO_2)

(a) Nitriding reactions are important in materials preparation and in their contamination by atmospheric nitrogen. For example, Pompe has used TG to investigate the nitriding kinetics of an iron alloy in N_2 [67] and the nitriding of a Mn-Si alloy in NH_3 [68]. Mumora and Ouchi [69] have used TG to follow the kinetics of nitriding of PuH_3 in NH_3.

(b) Uses of ammonium salts include propellants, refrigerants and catalyst precursors, and there have been several thermal analysis studies precursors, and there have been several thermal analysis studies in NH_3 atmospheres in these areas [70–72, 124]. An example is Stone's [73] use of DTA to demonstrate the strong influence of p_{NH_3} on the decomposition mechanism of the solid propellant NH_4ClO_4.

(c) Gimzewski and Hawking [74] have used combined TG + DTA to follow the reactions of several metal oxides with NO_2+O_2. The aim was to find reactions suitable for extracting metals from oxide ores.

4. *Carbon Dioxide*

(a) Carbonate decompositions are important in the building, ceramics, glass and chemical industries, in the burning of fossil fuels and in understanding geological processes [75]. In these cases, the minerals decompose in a self-generated atmosphere, so it is important to study them in CO_2 [76, 77]. As mentioned, this greatly improves the resolution of consecutive reactions, especially at high pressures, a point well illustrated in the DTA study of cerussite ($PbCO_3$) in 1–50 bar CO_2 by Yamaguchi *et al.* [78].

(b) Warne [79, 80] has used DTA in CO_2 to identify and quantify components in carbonate minerals at levels as low as 0.5%, claiming a better accuracy than by x-ray diffraction.

(c) Dobner *et al.* [20] have used TG with CO_2 pressures up to 4 bar to study the cyclic CO_2 acceptor reaction $CaO\cdot MgO_{(s)}+CO_2=CaCO_3\cdot MgO_{(s)}$ which is used in two coal gasification processes. Their kinetic study investigated variables like decomposition and formation temperatures, partial pressures of CO_2 and H_2O, number of cycles, and the extent of reaction.

(d) Honkins *et. al.* [81] have studied the corrosion of graphite nuclear fuel elements in low pressure CO_2. The surface area of the sample was measured gravimetrically in situ before and after the corrosion.

5. *Water Vapour*

(a) Mühlen *et al.* [82] have followed the kinetics of the steam gasification of char in the presence of H_2, CO_2 and CO at temperatures up to 1000° and pressures up to 70 bar.

(b) At the other extreme of pressure, Knudsen-effusion plus mass spectrometry with very low controlled pressures of H_2O or CO_2 was used to obtain thermodynamic data for the gasification of graphite-alkali metal systems [83]. This helped to elucidate the role of alkali salts as gasification catalysts.

(c) Rouquerol and co-workers [42–48] pioneered the decomposition of solids at low, constant rates in controlled pressures of the product gas; the temperature is varied to ensure a constant reaction rate. This technique has shown that the surface area of the alumina obtained by dehydrating gibbsite ($Al(OH)_3$) is 430 m^2 g^{-1} at 6.5×10^{-3} bar H_2O and 40 m^2 g^{-1} at $< 2.5\times10^{-5}$ bar. Significantly, in each experiment the surface area is a linear function of mass loss, indicating an unchanging reaction mechanism and a well-controlled dehydration. Another interesting effect of p_{H_2O} is on the crystallography of the product Al_2O_3. A completely amorphous alumina was obtained at $<5\times10^{-5}$ bar, a slightly crystalline beta alumina at $<1\times10^{-3}$ bar and a more crystalline chi alumina at < 1 bar. Moves towards the commercialization of this technique have been made by Fierro [48] and Stacey [125].

(d) Reversible dehydration reactions are exploited in some chemical heat pumps, and Anderson *et al.* [84] have used TG in $H_2O_{(g)}$ to study the reaction $BaCl_2 \cdot H_2O_{(s)} + H_2O_{(g)} = BaCl_2 \cdot 2H_2O$. They investigated the dependence of the reaction rate and extent on p_{H_2O}, temperature, number of cycles, time in the monohydrate form and the extent of dehydration.

(e) Using DTA or TG with an atmosphere containing H_2O, the dehydrations of $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot {}^1/_2 H_2O$ in plaster of Paris [85] are sharp and well-resolved, allowing $CaSO_4 \cdot 2H_2O$ to be quantified at levels usually undetectable by thermal analysis.

(f) The corrosion reaction, important in the nuclear industry, $Zr_{(s)} + 2H_2O_{(g)} = ZrO_{2(s)} + 2H_{2(g)}$, has been studied in TG apparatus which allows simultaneous beta irradiation [86] of the sample to simulate the real corrosion environment.

6. *Suphur Oxides*

(a) TG has been a major research tool in assessing regenerable absorbents for removing SO_2 [18, 87–91] and SO_3 [92] inside fluidized bed coal combustions. For example, O'Neil *et al.* [89] have used TG to follow reactions of limestone, decomposed limestone, dolomite and half-decomposed dolomite under the conditions of a pressurized fluidized bed combustor (730–950°, 1–10 bar, 0.1–0.5% SO_2, 3–12% O_2, 0–1.5 bar CO_2). The CO_2 suppressed the decomposition of the carbonate, therefore SO_x-carbonate reactions could be assessed and were found to be more attractive than SO_x-oxide reactions. Ulerich *et al.* [90] followed up this work with a study to compare the TG data with results from the Exxon pressurised miniplant.

(b) In one of the most ambitious uses of TG in this field (or any other) Ruth and Varga [18] assessed a large number of potential SO_2 absorbents, with particular attention to absorption capacity after many regeneration cycles.

(c) In extractive metallurgy, oxide and sulphide sulphation reactions occur in fluidized beds [94]. Hocking and Alcock [93] have used TG in a detailed study of the mechanism and kinetics of the reaction of Cu_2O with equilibrated $SO_2 + O_2$ mixtures.

7. *Hydrogen Suphide*

(a) Dobner *et al.*[20] and others [10, 95] have used high pressure TG to study both directions of the gas-cleaning reaction $CaCO_3 \cdot MgO_{(s)} + H_2S = CaS \cdot MgO_{(s)} + H_2O + CO_2$ under plant conditions. These were absortion at 750°C, 21 bar, 0.5% H_2S, 48% H_2, 5% CO_2, 46.5% N_2, and regeneration at 750°C, 21 bar, 40% CO_2, 50% H_2O, 10% H_2. The effects of repeated recycling (up to 30 times) showed that the extent of the forward reaction stabilized at 45% conversion.

(b) Nowak *et al.* [96] have studied the effect of the composition of brass on its sulphidation in H_2S+H_2, showing that the rate limiting step is cation diffusion through a sulphide layer.

8. *Chlorine-containing Atmospheres*

(a) In extractive metallurgy there have been many thermoanalytical (mostly TG) studies of oxides [97–102], sulphides [103–105] and silicates [14], pure and as minerals, and of metals [97, 98], in atmospheres such as Cl_2, Cl_2+CO, $COCl_2$, CCl_4, Cl_2+O_2, HCl, $FeCl_3$ and S_2Cl_2. For example, the reaction

$$Al_2O_{3\,(s)} \xrightarrow[1000^\circ]{C+Cl_2 \text{ or } CO+Cl_2 \text{ or } COCl_2\text{, etc}} 2AlCl_{3\,(g)}$$

has been intensively studied for extracting aluminium from various aluminas [106–111], kaolin [112], plagioclase [113], bauxite [114] and fly ash [114]. Here TG is ideal for assessing the reaction rate, selectivity and yield with various promoters (e. g.S, NaCl or BCl_3), types of carbons or other reducing agents (e. g.CO, CCl_4), or pretreatments.

(b) Nickl and v. Braunmühl [115] and Wiedemann [116] have accurately determined the stoichiometry of ceramic-grade carbides by following the weight loss in Cl_2 at 1000° (chlorination-vaporization of the metal component), then in O_2 at 600° (oxidation of the carbon residue).

9. *Fluorine-containing Atmospheres*

Most of the thermoanalytical studies in fluorine-containing atmospheres [3–5, 117–122] are of the actinide compounds used in the nuclear fuels industry. The TG studies include the reaction kinetics of F_2 with UO_2 [117], U_3O_8, UO_3 [118], PuO_2, UF_4, PuF_4 [119] and UC [120], of HF with UO_2 [121], and of ClF_3 with UF_4 [122]. Nikonorov *et al.* [3] have used DTA to follow many reactions of solids with F_2, ClF_3 and XeF_4, including those of the platinum group metals with F_2.

10. *Plasmas*

Gimzewski *et al.* [123] have compared the DC plasma and neutral gas hydriding of titanium to simulate the interaction of that metal with deuterium and tritium in proposed nuclear fusion reactors. The attainment of the equilibrium hydrogen concentration in the metal was ten times quicker in the DC plasma at the same temperature and hydrogen pressure.

Conclusions

Thermal analysis in reactive atmospheres is an important tool in research and development programmes in many branches of high temperature technology, particularly fuels (fossil, synthetic and nuclear). It is versatile and cost-effective, capable of obtaining fundamental data and of simulating many aspects of a commercial process quickly and with relatively little manpower. However, although its application to gas-solid reactions is widely appreciated, its role in studying decomposition reactions has only recently attracted attention from technologists despite the excellent pioneering work of Rouquerol and co-workers.

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Zusammenfassung – Das Anwendungsgebiet der thermischen Analyse wird durch Arbeiten in reaktiver Atmosphäre beträchtlich erweitert, so dass Hochtemperaturuntersuchungen auf solchen Gebieten wie Brennstoffe, extraktive Metallurgie, Material- und Katalyseforschung möglich werden. Dieser Übersichtsartikel behandelt die Konstruktion der Geräte und ihre Anwendungen bei kinetischen und thermodynamischen Untersuchungen in solchen Gasphasen wie H_2, CO, N_2, NH_3, CO_2, $SO_{2\,\mathrm{oder}\,3}$, H_2S, S_2, Cl_2, HCl, F_2 und HF sowie im Niederdruckplasma. Ausser Gas-Festkörperumsetzungen wird auch der Einfluss einer geregelten Produktgas-Atmosphäre auf Zersetzungsreaktionen diskutiert. Auf die Adsorption von Gasen an Festkörpern und Löslichkeitsuntersuchungen wird nicht eingegangen.

РЕЗЮМЕ — Область применения термического анализа при использовании реакционных газовых атмосфер может быть значительно расширена, включая многие аспекты высокотемпературных исследований топлив, металлургического извлечения, различных веществ и катализаторов. Приведено обозрение соответствующей аппаратуры и ее применения в кинетических и термодинамических исследованиях с использованием таких газовых атмосфер, как водород, фтор, хлор, окись углерода и двуокись углерода, аммиак, паров воды, двуокиси- и трехокиси серы, сероводорода, серы, фтористого и хлористого водорода при низком или высоком давлении, также как с использованием плазмы низкого давления. Помимо реакций газ — твердое тело, обсуждено также важное влияние на реакции разложения контролируемой образующейся газовой атмосферы. В обсуждение не включены исследования растворимости и адсорбции газ-твердое тело.