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A THERMOGRAVIMETRIC SYSTEM FOR INVESTIGATING GAS-METAL REACTION--ETC(U)

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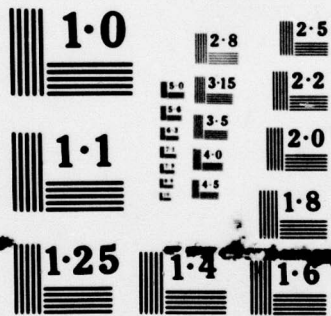
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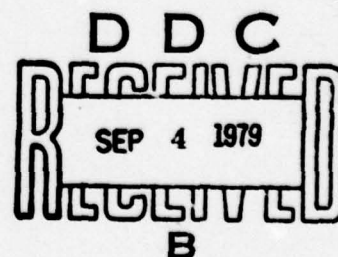
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A THERMOGRAVIMETRIC SYSTEM FOR INVESTIGATING GAS-METAL
REACTIONS AT ELEVATED TEMPERATURES

Lawrence D. Palmer

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REPORT

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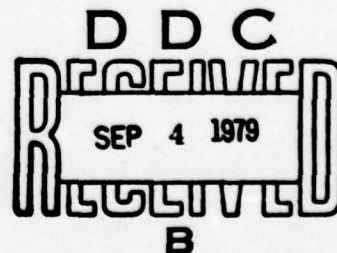
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ABSTRACT

This report describes the thermogravimetric system recently established at Materials Research Laboratories (MRL) to study the kinetics of reactions between solids and their gaseous environments at elevated temperatures. The rates of reactions, such as the high temperature oxidation of metals, are measured by continuously and automatically weighing samples during the course of the reaction. The basic components of the system are a sensitive electrobalance, which measures the changes in weight, and a furnace for elevating the temperature of the sample and its gaseous environment. The large-capacity (100 g) electrobalance is capable of detecting changes in weight as small as 2 μg , equivalent to oxide thicknesses of approximately 1.5 nm for samples with 10 cm^2 of surface area. The experimental conditions, particularly the hot gaseous environment, degrade this discrimination* by a factor of about 10. The effects which instability and non-uniformity of furnace temperatures have on the accuracy of the measurement of oxidation rate constants are discussed, as also are the advantages of differential thermopiles for assessing furnace temperature uniformity. Several furnaces have been shown to meet the stability and uniformity requirements.

A study has been made of the likely sources of error in the measurement of both weight and temperature. For the weight, the effect of angular movements of the wall on which the electrobalance is mounted have been assessed and these are shown to make only a small contribution to the limiting instability of the electrobalance output. The uncertainties of measurement caused by the hot gaseous environment, and by electrostatic and electromagnetic forces are also considered, in most cases quantitatively. Materials suitable for suspending hot samples from the electrobalance are considered, and polycrystalline alumina rods have been found to possess the required properties of high temperature strength and chemical inertness.

* BS 2643:1955, Definition No. 302

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A THERMOGRAVIMETRIC SYSTEM FOR INVESTIGATING GAS-METAL REACTIONS AT ELEVATED TEMPERATURES

1. INTRODUCTION

Thermogravimetric techniques provide a convenient, precise and widely used means of studying reactions between solids and their gaseous environments. For example, the rates of oxidation of metals and alloys at high temperatures can be determined by continuously weighing heated samples. Since oxidation at high temperature often limits the useful service lifetime of metals and alloys, and can seriously degrade their essential properties, thermogravimetric tests provide valuable information on the suitability of alloys for particular applications. In addition to determining reaction rates under specific conditions of temperature, pressure and gas composition, it is often possible to elucidate the basic mechanisms of the reactions. Examples are shown in Fig. 1, where the parabolic shape of the weight-time curve for a Ni-0.9%Si* alloy oxidized in air at 1373 K suggests (1) that the oxidation rate is determined by the rate at which the reacting ions diffuse through a compact, growing oxide layer which acts as a barrier separating the metal and oxygen; also the linear weight loss dependence on time for platinum is consistent with the formation of the volatile oxide PtO_2 (2).

To obtain an adequate understanding of the behaviour of materials in high temperature environments, the thermogravimetric data must be complemented by results from other techniques. Identification of the reaction products is necessary and, as in the case of the oxidation of Ni-0.9Si, information is needed also on such questions as whether metallic ions diffuse outward through the oxide layer to the oxide-air interface, or whether oxygen diffuses inward to react at the metal-oxide interface.

This report describes the thermogravimetric facility recently established at MRL to study the kinetics of the interaction of metals and alloys with gaseous environments at elevated temperatures. The equipment consists essentially of a recording electrobalance, which continuously measures weight changes, and a furnace capable of maintaining elevated temperatures

* In this report, alloy compositions are expressed as weight percentages.

constant and uniform for extended periods of time (>100 h). The use of the electrobalance for accurate weight-change measurements over extended periods and in close proximity to the furnace introduces several sources of error to the weight measurements. The resultant uncertainties of measurement are considered quantitatively in most cases. Such considerations generally point to those experimental techniques and arrangements which allow data of required accuracy to be gathered, as well as facilitating a reliable assessment of the capabilities of the system.

The MRL thermogravimetry facility has been set up to study the kinetics of high-temperature deteriorative processes to which materials of defence interest are prone when they are required to operate in high-temperature corrosive environments. These studies are directly relevant to Australian Defence in that, for example, the Armed Services are critically dependent on gas-turbine propulsion in aircraft and ships. The objective of these studies is to devise methods whereby the operational lifetimes and properties of components operating in such high-temperature environments can be extended, or the maximum operating temperatures increased. This work was done as part of DST Task No. R-05:DST 77/064.

2. THE THERMOGRAVIMETRIC EQUIPMENT

A schematic diagram of the MRL thermogravimetric system is shown in Fig. 2. At the heart of the system is a Cahn electrobalance, model RH, which continuously and automatically measures changes in the weight of samples suspended from it. The multi-zone furnace, suspended on a rail system allowing vertical movement, provides a high-temperature environment and promotes temperature uniformity in the samples under study. Specimen temperature is monitored continuously by an adjacent thermocouple. The nature and the performance characteristics of the various components of the system are discussed in greater detail in the following sections.

2.1 The Electrobalance

2.1.1 Operating principles

The operating principles of the Cahn model RH electrobalance are illustrated in Fig. 3. The sample and a counterweight are suspended from opposite ends of a beam assembly whose axis of rotation is defined by an elastic ribbon suspension. Attached to the beam is a coil located symmetrically in the magnetic field of a permanent magnet. Any imbalance of the torques due to the sample and the counterweight is dynamically balanced by an electromagnetic torque produced by current flowing through the coil. As the sample weight changes the beam tends to deflect, any deflection resulting in a change in the amount of light reaching a phototube. The amplified phototube current flows through the coil and maintains the beam in balance. The electromagnetic torque is linearly related to the coil current (Ampere's law), so that measurement of the changes in coil current, or voltage, effectively measures changes in sample weight.

To take advantage of the inherent high discrimination of this electromagnetic weighing system, a stable reference voltage is electrically subtracted from the coil voltage, and the difference voltage is measured by the chart recorder. The reference voltage is determined by the setting of a high-resolution ten-turn potentiometer (the MASS DIAL) which can be calibrated using standard masses to correspond, in terms of weight, to one of nine MASS DIAL RANGES extending from 10 mg to 20 g full-scale. The chart recorder which measures the difference voltage applied to it can also be calibrated in terms of weight, and by attenuating the difference voltage by known ratios (RECORDER RANGE switch) various weight ranges from 0.2 mg to 20 g full-scale can be utilized.

For lengthy experiments during which the system is unattended for extended periods (e.g., overnight) the discrimination of the system described above is often limited by the low dynamic range of the chart recorder (i.e., the ratio of its full-scale voltage to its minimum resolvable voltage). The complementary use of a 5½-digit voltmeter has solved this problem (ref. Fig. 3). The three least-significant figures from the digital voltmeter are converted to an analogue signal for the chart recorder, thereby increasing the dynamic range of the system by a factor of 200. This modification is the first step in the eventual introduction of microprocessor control and automatic acquisition of weight, temperature and time data.

2.1.2 Electrobalance accuracy for oxidation studies

The rates of gas-metal reactions at high temperatures are generally measured in terms of weight change per unit of surface area. The ability of the electrobalance to accurately monitor all stages of processes such as high temperature oxidation therefore depends basically on the discrimination of the balance, the balance capacity (maximum sample weight), and the sample geometry, which determines the surface area to weight ratio. High surface area to weight ratios can be achieved with thin specimens, but a minimum limit on thickness is imposed by the requirement that the core of the specimen shall be unreacted at the end of the experiment. For example, oxidation tests of 200 h duration on nickel-base alloys at a temperature of 1400 K usually require samples at least 1 mm thick.

The Cahn model RH electrobalance has a capacity of 100 g, which permits samples of relatively high surface area to be studied with little restriction on the sample geometry. According to the manufacturer, the discrimination of the balance is the largest of the values -

- (i) 1% of the most sensitive RECORDER RANGE, i.e. 2 µg,
- (ii) 10^{-7} of the sample weight, and
- (iii) 10^{-4} of the maximum anticipated weight change, i.e. of the selected MASS DIAL RANGE.

The electrobalance therefore is capable of measuring weight changes as small as 2 µg, provided that the sample weight is less than 20 g and the total weight change to be measured in the experiment is less than 20 mg. The ultimate accuracy of the system is therefore >2 µg.

A better appraisal of the capability of the electrobalance to accurately measure the rates of gas-metal reactions can be obtained by estimating, on an atomic scale, the thickness of oxide equivalent to a weight increase of 2 μg caused by oxidation. Consider a layer of oxide with the chemical formula M_xO_y formed on a metal M. The weight of this oxide can be written

$$W = \rho_{\text{ox}} A d_{\text{ox}} \quad (1)$$

where ρ_{ox} is the density of the oxide, A is the surface area of the oxidizing metal, and d_{ox} is the oxide thickness. Of this weight, only the oxygen component ΔW_{ox} is registered by the electrobalance, and

$$\Delta W = 16 y \rho_{\text{ox}} A d_{\text{ox}} / m_{\text{ox}} \quad (2)$$

where m_{ox} is the formula weight of the oxide M_xO_y . Table 1 gives values, for several metals, of the oxide thickness d_{ox} corresponding to a weight gain of 2 μg on a sample of surface area $10^{\text{ox}} \text{cm}^2$, which is a typical and convenient sample surface area for the system shown in Fig. 2. Also included in Table 1 are the corresponding regressions d_m of the substrate metals calculated from the following equation -

$$(x m_m / 16 y) \Delta W = \rho_m A d_m \quad (3)$$

where m_m and ρ_m are the atomic weight and the density of the metal.

If the values of d_{ox} and d_m from Table 1 are compared with ionic radii (e.g. 0.07 nm for Ni^{2+} , 0.13 nm for O^{2-}), it can be seen that the electrobalance is capable of resolving weight changes equivalent to a few atomic layers of oxide. It must be remembered, however, that the experimental conditions usual for studies of high temperature oxidation are unfavourable for highly accurate weight measurements. To realize the rated discrimination of the electrobalance in the presence of the electrical noise which usually accompanies the electrobalance output signal in high temperature studies (see Section 3), filters with extremely long time constants are needed. The slow response of these filters will often prevent the measurement of rapid weight changes.

2.2 Furnace Requirements

The most important characteristic of a furnace for thermogravimetric studies is its ability to provide a region of high temperature which is spatially uniform around the specimens and which is constant during experiments. For high-temperature oxidation reactions in isothermal atmospheres, the required degree of stability and spatial uniformity of temperature can be estimated by considering the variation of reaction rates with temperature.

For many metals the weight gain due to high temperature oxidation has an approximately parabolic dependence on time. The parabolic equation is

$$(\Delta W)^2 = k t \quad (4)$$

The parabolic rate constant k obeys an Arrhenius equation

$$k = A \exp(-E_a / R T) \quad (5)$$

where E_a is the activation energy for the process controlling the oxidation rate, T is the temperature, R is the gas constant, and A is a quantity approximately independent of temperature. Differentiating eqn. (5) with respect to temperature gives

$$dk/dT = (E_a / R T^2) \exp(-E_a / R T) = E_a k / R T^2 \quad (6)$$

For small changes ΔT in T , the corresponding change Δk is therefore given by eqn. (7)

$$\Delta k / k = E_a \Delta T / R T^2 \quad (7)$$

This equation can be used to estimate the uncertainties Δk , due to temperature variation, in experimentally derived values of k . Alternatively, eqn. (7) can give the maximum allowable temperature variation for experiments designed to yield parabolic rate constants of specified accuracy. Consider, for example, the oxidation of nickel in oxygen at a pressure of 1.0×10^5 Pa and at 1373 K, for which $E_a = 183 \text{ kJ mole}^{-1}$ (3). If errors in k caused by temperature variations are to be less than $\pm 1\%$, eqn. (7) requires that variations ΔT in the temperature be

$$\Delta T < 0.9 \text{ K}$$

Because the magnitudes of E_a for many other systems do not differ from the nickel value by a factor more than two, it can be concluded generally that temperature uniformity of ± 1 K is required to obtain parabolic rate constants with errors due to this cause of less than about $\pm 1\%$. For most previous thermogravimetric studies, overall temperature variations have been much greater than ± 1 K. The present work, however, shows (Sections 2.5 and 2.7) that temperature control of ± 1 K is attainable; the resultant small uncertainty in oxidation rates facilitates studies of the influence of other parameters, e.g. sample preparation and purity (4), on oxidation rates.

2.3 Hot-Corrosion Furnace

The furnace used for initially assessing the capabilities of the MRL thermogravimetry system, and for some early oxidation experiments on nickel-silicon alloys, is shown schematically in Figs. 2 and 4. This furnace was designed at MRL, and was intended for studying by thermogravimetric means the hot-corrosion reactions which occur in marine gas turbines. There are three work-zones, each resistively heated by metallic elements wound on a single alumina tube of 44 mm O.D. The top (reaction zone) element is Pt-20Rh and the two lower zones, which were designed to preheat upwardly-flowing reactant gas and to vaporize into this gas stream solids such as sodium salts, are heated by Ni-20Cr elements.

... The temperature at the centre of each of the three windings can be maintained constant by a control thermocouple (Pt-13Rh/Pt) actuating a highly stable temperature controller of the proportional-integral-derivative type (5). To attain particular temperature gradients along the furnace tube, the ratio of the heating currents in each half of particular zones can be adjusted by variable autotransformers in the primary circuits of the step-down transformers (see Fig. 4).

Fig. 4 also shows typical temperature gradients in the reaction zone of the hot-corrosion furnace when the settings of the temperature controllers and the autotransformers are optimized to produce a long, uniform-temperature region. For temperatures up to 1380 K regions with temperature variations less than ± 1 K over 10 cm are found, so that relatively large thermogravimetric samples can be easily and satisfactorily positioned. At temperatures above 1380 K, the length of the uniform temperature zone decreases because of a limit of ~ 1380 K on the operating temperature of the Ni-20Cr windings heating the lower two zones. The Pt-20Rh element itself can operate at 1850 K, but because the adjacent part of the Ni-20Cr winding must not be overheated, 1470 K is the highest temperature for which a useful uniform temperature region in the upper zone can be established.

Contrary to expectation, it was the failure of the Pt-20Rh zone rather than the adjacent Ni-20Cr zone which ended the life of this multi-zone furnace element. At burn-out, the thermal history of the Pt-20Rh zone was :

600 $\pm$ 100 h at 1470 K

4200 $\pm$ 200 h at 1380 K and

$\sim$ 1200 h at $\leq$ 1270 K

Inspection of the Pt-20Rh element after its failure showed that the diameter of the wire was substantially reduced in several places, and that small crystals were deposited on the adjacent element support-tube and alumina embedding cement. This mode of failure for Pt-Rh furnace elements has been observed previously at MRL. Together with our experience with the base-metal furnace element material 'Kanthal A1' (Fe-22Cr-5.5Al-0.5Co), these observations lead to the conclusion that for temperatures ≤ 1520 K, this base-metal material is preferable to Pt-20Rh from both lifetime and cost aspects.

2.4 Nicrosil Furnace

Following the failure of the Pt-20Rh furnace element a new furnace element was constructed at MRL, from an alloy (Ni-13.9Cr-1.5Si) similar to the thermocouple alloy Nicrosil, and was incorporated in the original furnace. Nicrosil has very high oxidation resistance (6) and a Nicrosil-type alloy was immediately available as wire of diameter 1.6 mm, which provided a furnace element whose electrical resistance was compatible with the power supplies of the original furnace. The use of this alloy also provided an opportunity to assess the suitability of Nicrosil as a furnace element material.

Fig. 5 shows the temperature gradient in the Nicrosil furnace at 1373 K, after the settings of the temperature controllers and autotransformers (see Fig. 4) have been optimized to produce an extensive region of uniform temperature. As in the hot-corrosion furnace, the extent of the uniform-temperature zone allows relatively long samples to be easily and satisfactorily positioned for thermogravimetric tests.

The Nicrosil furnace failed after 4700 h (6.4 months) of operation at 1373 K, by a fracture in the middle-element winding. This lifetime compares favourably with that of the Pt-20Rh winding of the hot-corrosion furnace, but is shorter than the lifetime of the 'Kanthal Al' element which superseded the Nicrosil element.

2.5 'Kanthal Al' Furnace

The furnace element material for the furnace currently in service is the alloy 'Kanthal Al' (Fe-22Cr-5.5Al-0.5Co). The power and temperature-control circuitry for this furnace is shown in Fig. 6 together with the optimum temperature gradients for isothermal thermogravimetry. The power and temperature control circuit shown in Fig. 4 has been modified significantly, for use with this furnace, by using a single pyrometer to control the temperature of all six half-zones via triacs. This modification was made to facilitate the incorporation of a programmable linear ramp-generator (7) whose millivolt output is added to that of the control thermocouple, and which permits thermogravimetric tests to be performed, if desired, under conditions of specific linear variations of temperature. Compared with the original control system shown in Fig. 4, the present system has reduced capability for precise control of the temperature gradients in the vicinity of test specimens under conditions of varying gas flow, because of the elimination of two of the three points of precisely controlled temperature.

With the linear ramp generator, the furnace temperature can be programmed to vary at particular rates, enabling assessment to be made of alloy properties such as oxidation resistance under changing temperature conditions. Thermal activation energies for oxidation reactions can thereby be determined (8) more conveniently than by performing several isothermal experiments at selected constant temperatures. Useful information can be obtained also on the oxidation behaviour of alloys whose oxides spall at characteristic temperatures during cooling from high temperature (9).

An upper limit on the heating rate under the control of the ramp generator is imposed by the maximum available furnace power, while the most

rapid controlled cooling rate is governed by the natural cooling rate of the furnace. Alloy oxidation-kinetics experiments have been performed (9) over the temperature range 1123-1523 K with a ramping rate of $14 \mu\text{V min}^{-1}$, which is close to the upper heating rate limit. Because the Seebeck coefficient for the Pt-13Rh thermocouple is not constant throughout this range, the corresponding heating rate ranges from 1.12 K min^{-1} at 1123 K to 1.00 K min^{-1} at 1523 K.

When the furnace temperature is 'ramped', it is important to establish that the temperature gradient across the sample remains acceptably low at all temperatures. Because of the large thermal capacity of the furnace (see Fig. 2), periods of several hours generally are required for the gradient to reach its steady state. The steady-state gradients presented in Fig. 6 for 1173 and 1473 K, therefore, cannot be assumed to apply rigorously under ramping conditions. Nevertheless at a ramp-rate of $14 \mu\text{V min}^{-1}$, the gradient across a 35 mm-long sample is $<2.5 \text{ K}$ for all temperatures in the range 1173-1523 K.

2.6 Molybdenum Furnace

In order to increase the maximum operating temperature of the thermogravimetry system from 1520 K to about 2100 K, a molybdenum-wound furnace is currently being constructed (10).

2.7 Long-term Temperature Stability

The stability of the temperature in the Kanthal Al furnace near the thermogravimetric samples is exceptionally high for both short- and long-term ($>100 \text{ h}$) experiments. This stability is due primarily to the performance characteristics of the temperature controllers (Section 2.3) and to the nearly constant heat losses from the furnace when operating isothermally in an air-conditioned laboratory. For oxidation experiments at 1373 K, the measured temperatures vary by $<1 \text{ K}$ from the mean during 160 h experiments.

2.8 Temperature Measurement

Specimen temperatures are measured by an adjacent Pt-13Rh thermocouple (Figs. 2 and 8) which actuates an electronic digital thermometer (Doric Trendicator 400A). The output of the thermometer is converted to an analogue signal for display on the two-pen chart-recorder which simultaneously records weight changes.

Another aspect of the temperature measurements requiring careful attention is the assessment of gradients in the reaction region in which the samples are located. A novel approach to this problem is the use of a differential thermopile (Fig. 8), which allows a direct measurement of the temperature differences between the junctions. Compared with the alternative technique of measuring temperatures at different positions with a conventional thermocouple, the multi-thermojunction technique is more convenient and more accurate for determinations of temperature differences. Additional discussion on the accuracy of temperature measurements is presented in Section 3.4.

2.9 Suspension of Hot Samples from the Electrobalance

There are three essential requirements of the system used to suspend the hot samples :

- (i) Its rate of weight change must be known under the experimental conditions; in practice, a material is used whose rate of weight change, for example by vaporization or by interaction with the gas phase, is very small compared with the rate of weight change of the samples under study.
- (ii) It must be inert with respect to the material under study; the possibility of the occurrence of solid-state reactions between the suspension and the sample, at their region of contact or via the gas phase, or of gas-solid reactions, must be virtually eliminated.
- (iii) It must have sufficient strength and creep resistance to support the samples at high temperatures for experimental periods of typically 200 h.

Because the sample materials of greatest practical interest for thermogravimetric study often have high oxidation resistance, requirement (i) is satisfied by very few materials. Platinum seems to be the most commonly used suspension material, possessing sufficient strength up to 1800 K. Recent reports (e.g. 11,12) indicate, however, that platinum does influence oxidation rates in some cases. Furthermore, the oxidation rate of Nisil (Ni-4.4Si-0.1Mg) has been shown at MRL (13,14) to be accelerated by platinum, and in the present work weight changes of approximately $4 \mu\text{g cm}^{-2} \text{ h}^{-1}$ have been measured for platinum at a mean temperature of 1400 K, under zero gas-throughput conditions.

Fibres and rods of sapphire, polycrystalline alumina and silica have been used by other workers, with single-crystal sapphire being suitable for very high temperature work to 2070 K (15). These materials are ideally suitable for suspensions because of their chemical stability at high temperature, but they present some problems in fabrication of hooks for joining to the samples.

The suspension system which is used for thermogravimetry at MRL is illustrated in Fig. 8; it operates reliably for extended periods at temperatures at least as high as 1520 K. It is constructed from alumina rods and a small length of an alumina four-hole thermocouple insulator. Hooks are fabricated by heating the rod to near its melting point with a very fine oxy-hydrogen flame.

3. SOURCES OF ERROR IN THERMOGRAVIMETRY

3.1 Drifts in Electrobalance Readings at Room Temperature

Although the major uncertainties in thermogravimetric weight measurements are caused by the high temperature environment of the samples, there are other factors which can produce weighing errors, even at room temperature. The manufacturer's claim that the Cahn RH electrobalance can discriminate weight changes as small as $2 \mu\text{g}$ was discussed in Section 2.1. The filter circuits at the electrobalance output, with time constants of a few seconds, do indeed reduce the electrical noise accompanying the output signal to a level where $2 \mu\text{g}$ is easily resolved on a chart recorder. However, slow drifts in the output of the electrobalance under constant weight load are observed, and because oxidation experiments often extend beyond 100 h, even small drifts at constant load may produce significant errors in the measured weight changes. Typical drift rates have been determined and, so that they can be minimized, a considerable effort has been made to identify their causes.

Fig. 7 shows that the slow drifts comprise -

- (i) a drift showing a 24 hour cyclic variation superimposed on
- (ii) an extended slower drift with variable magnitude and direction.

It seems clear that the diurnal drifts result mainly from the effects of room temperature variations on the electrobalance. In Fig. 7(a) the maxima in the electrobalance output lag behind the minima in room temperature by ~ 4 h, partly due to the insulating effect of the aluminium-foil covered glass-bottle which houses the balance assembly, and partly due to the relatively large thermal capacity of the balance assembly. From Fig. 7(a), and other results, the temperature coefficient of the diurnal drift is $-7 (\pm 2) \mu\text{g K}^{-1}$. This temperature coefficient can be electrically compensated by a thermistor mounted on the weighing mechanism, or minimized by controlling ambient air temperature variations within close limits. Fig. 7(b) shows a typical result obtained after compensation. The peak-to-peak magnitude of the daily cycle has been attenuated, but not eliminated.

Attempts to eliminate completely the diurnal drifts when the electrobalance was in its original location (Room 527 of Building 680) were unsuccessful, because the more random drifts (see Fig. 7(b)) made it difficult to estimate the actual value of the temperature coefficient. Furthermore, variations in room temperature produce changes in the electrobalance output in several different ways. For example, apparent weight changes occur if either the balance assembly or its control unit is subjected to a local temperature change. A further contribution to the diurnal drift is caused by any temperature-induced variation in the tilt of the wall on which the electrobalance is mounted (16). It is likely that there are phase differences between the various components contributing to the total diurnal drift, and such phase differences make complete elimination of the cyclic drift, by a single compensator mounted on the balance assembly, virtually impossible.

These considerations, and the rise in room temperature produced when the furnace is at elevated temperatures, show that it is necessary to locate the system in an air-conditioned laboratory. In its new location (Room 524 of Building 680) room temperature, and hence the ambient environment of the balance, is stable to within ± 1 K. Whereas the former laboratory (Room 527) is located on the north-facing side of the building, the latter laboratory (Room 524) faces south, and so absorbs less direct solar radiation during the summer months when diurnal ambient temperature variations are greatest. Since the daily cycle of tilt of the wall on which the electrobalance is mounted should consequently be substantially less in the new location, this factor also should reduce the diurnal drift of the electrobalance output.

The drift in electrobalance output shown in Fig. 7(c) is a selected 'worst case' for the balance located in the air-conditioned laboratory. More typical behaviour is presented in Fig. 7(d). The causes of the spikes and step-changes remain unknown, due to their low frequency of occurrence. At the University of New South Wales, other workers (17) have experienced similar problems with Cahn RH electrobalances. When continuous weight changes are being measured (e.g. during oxidation experiments) the step changes are readily identified and the data can be corrected. The slower drifts are more insidious because they generally cannot be distinguished from the weight change of interest. Measurement of drift rates before and after each experiment provides an approximate means of correcting for the slow drift. Alternatively, the high load-capacity of the electrobalance (up to 100 g) can be exploited so that the drifts are an insignificant fraction of the true weight change of interest.

An investigation has been made of the changes in the weight indicated by the electrobalance when its inclination is changed. Together with measurements of the variation in the tilt of the wall on which the electrobalance is now mounted, this information provides an estimate of the characteristic errors which movements of the mounting wall produce in the thermogravimetric measurements.

To measure the apparent weight change as a function of electrobalance inclination, the electrobalance was stood on a platform whose inclination to the horizontal plane is defined in Fig. 9(a) by the angles θ' and ϕ which measure the rotation of the platform about horizontal axes perpendicular to the electrobalance beam for the case of θ' , and parallel to the beam for case ϕ .

The functional dependence of the electrobalance output (i.e. of the indicated weight) on θ' can be derived by considering the mechanics of the system. (Such a consideration also provides a useful insight into the design and operating principles of the Cahn RH electrobalance, which were outlined in Section 2.1). In Fig. 9(b), A and B are the points on the beam from which the sample of weight W_s and the counterweight W_c are suspended. The beam weight W acts through its centre of gravity G , and the beam is supported by a taut ribbon at C. With AB inclined at an angle θ to the horizontal, taking moments of the forces about the axis of rotation through C gives

$$W_s l \cos \theta - W_c l \cos \theta + W_s d \sin \theta + W_c d \sin \theta + W h \sin \theta - T_e - T_r = 0 \quad (8)$$

where T_e is the electromagnetic torque which serves as the basic measurement of weight change, and T_r represents the torque applied to the beam by the ribbon suspension. T_r is small and independent of θ when $W_s - W_c$ is constant.

Because the quantity of light reaching the photocell must remain nearly constant for particular values of $W_s - W_c$, tilting the beam support system and photocell assembly (see Fig. 3)^s necessarily produces an equal change in the beam inclination θ , i.e. to a first approximation,

$$\theta' = \theta + \text{constant} \quad (9)$$

The value of the constant depends on $W_s - W_c$, being close to zero when $W_s - W_c = 0$ and having a maximum value of $\sim 1.2^\circ$ when $W_s - W_c = \pm 10$ g, the weight equivalent to the largest torque the electrobalance can produce.

Differentiating eqns. (8) and (9) yields

$$\partial T_e / \partial \theta' = \partial T_e / \partial \theta = - (W_s - W_c) l \sin \theta + [(W_s + W_c)d + Wh] \cos \theta \quad (10)$$

As the electromagnetic torque T_e is calibrated in terms of weight, eqn. (10) describes the variation of apparent weight with electrobalance inclination θ' .

Experimental measurements of apparent weight as a function of electrobalance inclination are shown in Fig. 10. As expected from eqn. (10), the apparent weight varies linearly with θ or θ' when $W_s \approx W_c$ and $|\theta'| < 1$ deg. The linear variation is observed for $|W_s - W_c| \lesssim 1.5$ g.^c For greater differences between W_s and W_c , the slope $\partial T_e / \partial \theta'$ is not constant because the $\sin \theta$ term in eqn. (10) becomes significant e.g. curve D in Fig. 10. Consideration of the data presented in Fig. 10, together with eqns. (9) and (10) leads to the conclusion that

$$\partial T_e / \partial \theta' < 10 \text{ mg deg}^{-1}, \text{ for } -1 < \theta' < 1 \text{ deg and } W_s + W_c < 100 \text{ g} \quad (11)$$

Changing the electrobalance inclination by varying the angle ϕ (see Fig. 9(a)) produces changes in the apparent weight smaller than those produced by changes of θ' . Measurements made with $W_s + W_c < 16$ g and $W_s - W_c \leq 4.5$ gave

$$\partial T_e / \partial \phi < 1 \text{ mg deg}^{-1} \quad (12)$$

The results above show that when highly precise thermogravimetric data are required, it is important to ensure that the electrobalance performance is not degraded by angular movement of its supports (i.e. changes in θ' and ϕ). For short-duration (<1 hour) experiments the manufacturer claims that data with precision of 2 μg can be obtained, while for long-term experiments (1-10 days duration), the precision is degraded to 20 μg . The maximum acceptable angular movement of the electrobalance supports can be specified in terms of these precision ratings. If angular movement is to contribute <30% to the total uncertainty in the weight measurement, the stability of the electrobalance supports must be $\Delta\theta' < 0.2''$ and $\Delta\phi < 2''$ for short-term experiments, while for long-term experiments the stability required is $\Delta\theta' < 2''$ and $\Delta\phi < 20''$.

Measurements of the changes in the tilt of the wall (in Room 524) on which the electrobalance is now mounted are presented in Fig. 11, together with the simultaneous electrobalance output under constant weight load conditions. The tilt measurements were made with a Talyvel electronic level fixed to the electrobalance mounting bracket. Diurnal cycles in the wall inclination of $\pm 1''$ peak-to-peak in the angle θ' , and $\pm 4''$ in ϕ , were detected, superimposed on a slow drift which may originate in the Talyvel electronics. Using the measured values for $\partial T / \partial \theta'$ and $\partial T / \partial \phi$, the corresponding peak-to-peak values of the apparent weight cycles are smaller than $\pm 3 \mu\text{g}$ and $\pm 1 \mu\text{g}$ respectively. From the foregoing discussion, and from Fig. 11, it can be seen that cyclic weight variations of this magnitude do not significantly increase long-term uncertainties in electrobalance weight measurements.

For short-term thermogravimetric experiments, the apparent weight changes calculated from the inclination changes are generally smaller than $\pm 2 \mu\text{g h}^{-1}$ for changes in θ' , and smaller than $\pm 0.5 \mu\text{g h}^{-1}$ for changes in ϕ . It is concluded that, while the stability of the electrobalance output is sensitive to changes in the tilt of the wall on which it is mounted, the wall actually chosen for mounting the electrobalance has a stability sufficient for operating the electrobalance close to its rated precision.

3.2 Forces Exerted by the Hot Gaseous Environment

When a thermogravimetry sample is suspended in a heated gas various disturbing forces act on it which in most cases determine the limiting precision of the electrobalance. These forces can be divided into three groups, which are briefly discussed below :

3.2.1 *Buoyancy forces*

A thermogravimetry sample is subject to an upthrust or buoyancy equal to the weight of gas it displaces. An apparent weight change therefore occurs when the density of the gaseous environment of the sample changes. The sample weight must be corrected, therefore, whenever changes are made in the reaction temperature, pressure or gas composition. Even when a study is performed with these three parameters held constant, buoyancy forces must not be neglected, because the experiment usually is initiated by rapidly changing one of these parameters. The experimental difficulty arises because of the finite time, generally of the order of a minute, required to establish the desired experimental conditions. During this time the electrobalance indicates the combined weight changes caused by changes in buoyancy and by the early stages of the reaction under study.

The buoyancy correction can be readily calculated from the ideal gas equation, and its importance can be assessed relative to the weight change occurring in a particular experiment. For a sample of volume 1 cm^3 , for example, the upthrust decreases by $\sim 1 \text{ mg}$ (from 1.21 to 0.28 mg) on heating in air from 293 to 1273 K. This apparent weight change is very large compared with the smallest detectable weight changes given in Section 2.1.1.

3.2.2 Forces of thermal motion

The effects of gas thermal motion on electrobalance measurements have been studied by several workers (18-20). The two types of perturbing force which have been found to be the most significant are :

- (i) Knudsen forces, which for air are detectable in the 10^{-7} to 10^2 torr (10^{-5} to 10^4 Pa) for conventional electrobalances (18). These forces are the result of differences in the mean momentum of gas molecules bombarding both the sample and suspension in the temperature gradient. These differences produce a resultant force on the sample and suspension. Maximum values of several milligrams weight occur at pressures around 10^{-1} torr (10 Pa) (18), when the mean free path of the gas molecules becomes comparable with the distance from the suspended sample to the reaction tube wall. For accurate thermogravimetry, Knudsen forces can be reduced by minimizing temperature gradients in the region of the samples under study, and by using small diameter suspension fibres.
- (ii) Convection forces, which in thermogravimetry are observed at pressures above about 100 torr (10^4 Pa) (18). This aerodynamic force has two components - one producing a constant offset in apparent weight, and the other, usually described as aerodynamic noise, being a fluctuating force with a broad frequency spectrum. The peak-to-peak noise it produces in the electrobalance output increases together with - (i) the temperature of the gases surrounding the sample and suspension; (ii) the pressure of the gases, an increase from 20 to 70 kPa increasing the noise by a factor of 20 (19); (iii) the internal diameter of the reaction tube surrounding the sample and suspension, the noise increasing rapidly for tube diameters above 20 mm (16); (iv) the horizontal surface area of the samples (19); and (v) the reciprocal of the measurement system response time, i.e. the noise can be reduced by electronic filters. Using a reaction tube with 25 mm I.D. in atmospheric pressure and filter time constant of 2 s, typical noise levels at the electrobalance output are $< 2 \text{ } \mu\text{g}$ peak-to-peak from 290 to 470 K, $12 \text{ } \mu\text{g}$ at 570 K and $25 \text{ } \mu\text{g}$ at 1270 K.

3.2.3 Forces from gas throughput

The forced flow of gas past the sample and suspension not only influences the rates of some reactions involving gaseous products or reactants (e.g. the oxidation of platinum, and of NiSiI suspended by platinum), but the resulting forces also affect the apparent weight of samples. For example, for a reaction temperature of 1373 K, the flow of air, which results with the present system from uncoupling the reaction tube from the water-cooled union (Fig. 2) while constricting the flow by inserting at the base a tube 7 mm diam.

and 130 mm long, reduces the apparent weight of a 3 mm diam. cylindrical sample by ~ 6 mg. This flow also increases the peak-to-peak aerodynamic noise by a factor of three compared with no-flow conditions. For accurate thermogravimetry, it is essential to avoid random changes in gas throughput.

The discussion above provides a basis for choosing experimental conditions for which aerodynamic noise is tolerably low. For the combined effects of the more constant components of the perturbing forces produced by the gaseous environment, the necessary weight corrections to the electrobalance readings can be determined experimentally. For example, in those high-temperature oxidation experiments which are initiated by raising the preheated furnace to surround the suspended samples and heat them to the reaction temperature within a few minutes, the corrections can be estimated from similar preliminary experiments using inert samples (e.g. alumina) which have the same shape as the samples to be studied subsequently. A typical set of results is shown in Fig. 12, in which the weight changes are relative to the electrobalance weight reading when the samples are at room temperature. The results for the inert samples are the average of two experiments, and the bars indicate the deviation of the individual results. Fig. 12 shows also the apparent weight of three Ni-3.1Si samples which begin to oxidize rapidly at approximately 970 K. It can be seen that a temperature-dependent correction to the weight-gain data is required during the early stages of oxidation when the combined effects of buoyancy and convection have not stabilized.

3.3 Electromagnetic and Electrostatic Forces

The magnetic field produced by the furnace heating current exerts a relatively strong force on ferromagnetic samples suspended in the furnace. For nickel and nickel-silicon alloys, however, whose Curie temperatures are ≤ 631 K, the samples become paramagnetic well below temperatures of interest for high temperature oxidation studies. Apart from an initial perturbation as the samples are heated to their Curie temperature in these cases, the magnetic field does not introduce any uncertainty into the measurement of the weight change. For elements (e.g. iron and cobalt) and alloys with high Curie temperatures, some uncertainty would result from the small variations in the furnace heating current which occur even during isothermal experiments.

Electrostatic forces have been found to introduce uncertainty into electrobalance measurements only when glass components, e.g. sample trays are suspended. The use of alumina suspension rods inside alumina furnace tubes does not produce detectable electrostatic forces.

The use of aluminium foil to cover the glass envelope (Fig. 2) is a recommended practice. As well as functioning as an electrical shield for the electrobalance beam assembly and the electronic components in the envelope, the foil protects the photocell from stray light, and provides additional thermal insulation.

3.4 Minimizing Temperature Errors

In Section 2.2 it was shown that for accurate measurement of oxidation rate constants, the spatial and temporal variations of the temperature of the sample should be smaller than ± 1 K, and its temperature level must be accurately known. Careful and accurate temperature measurement techniques are therefore essential. The following discussion gives the methods used at MRL to minimize temperature errors.

The Pt-13Rh/Pt thermocouples used for measuring sample temperatures are calibrated prior to use by the CSIRO National Measurement Laboratory. The thermo-electromotive force (E) versus temperature calibration is uncertain within $\pm (2 + 0.001 E)$ μV , equivalent to ± 1.0 K at 1400 K. During subsequent use, a slow drift in E occurs, typically of the order of 10 nV h^{-1} at 1400 K for thermocouples made from 0.25 or 0.50 mm diameter wire. Because the drift rate cannot be reliably predicted, the total drift (ΔE) after approximately 700 h at high temperature is measured by electrical intercomparison with a new, calibrated Pt-13Rh/Pt thermocouple. This measurement must be performed with the two thermocouples in the same temperature gradient in which the older thermocouple has been operating, because ΔE is primarily due to the development of chemical inhomogeneity in the hot sections of the Pt-13Rh wire (21), and it is dependent on the temperature gradient along the wire. For similar reasons, ΔE measured at a particular temperature may not necessarily apply at other temperatures. Care should also be taken to avoid contaminating and straining the wires during assembly and installation of thermocouples. After measuring ΔE at 700 h, the temperatures for prior thermogravimetric experiments can be estimated with sufficient accuracy by assuming that ΔE is a linear function of time. Further measurements of ΔE are made after approximately 1400 and 2000 h at high temperature. Thermocouples are replaced after 2000 h because of the increasing effects of chemical inhomogeneity and because grain growth in the platinum wire increases the likelihood of fracture.

Further uncertainty in the measured temperature arises when the length of the uniform temperature region (Figs. 4-6) is small, and when large diameter thermocouples are used. With these conditions, heat conduction along the thermocouple may produce a low temperature reading. One 'rule-of-thumb' states that the thermocouple diameter should be less than one tenth of the length of the uniform temperature region. A useful practical test for a particular diameter thermocouple is to replace it with one whose diameter is less than one half that of the original. If the same temperature reading is obtained after applying calibration corrections to both, the heat-conduction error is negligible. The thermocouples used for thermogravimetry (Fig. 8) satisfy this test.

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T A B L E 1

ELECTROBALANCE CAPABILITY FOR DETECTING
OXIDE GROWTH ON METALS

Metal/ Metal Oxide	Oxide Density* g cm ⁻³	Min. Detectable Oxide Thickness**, nm	Min. Detectable Metal Regression**, nm
Si/SiO ₂	2.2-2.7	1.4-1.7	0.75
Ni/NiO	6.67	1.4	0.82
Co/CoO	6.45	1.5	0.83
Al/Al ₂ O ₃	3.97	1.1	0.83
Cr/Cr ₂ O ₃	5.21	1.2	0.60

* Room temperature values; Handbook of Chemistry and Physics, 56th Edition, 1975-6.

** Assuming uniform-thickness oxide on samples of surface area 10 cm².

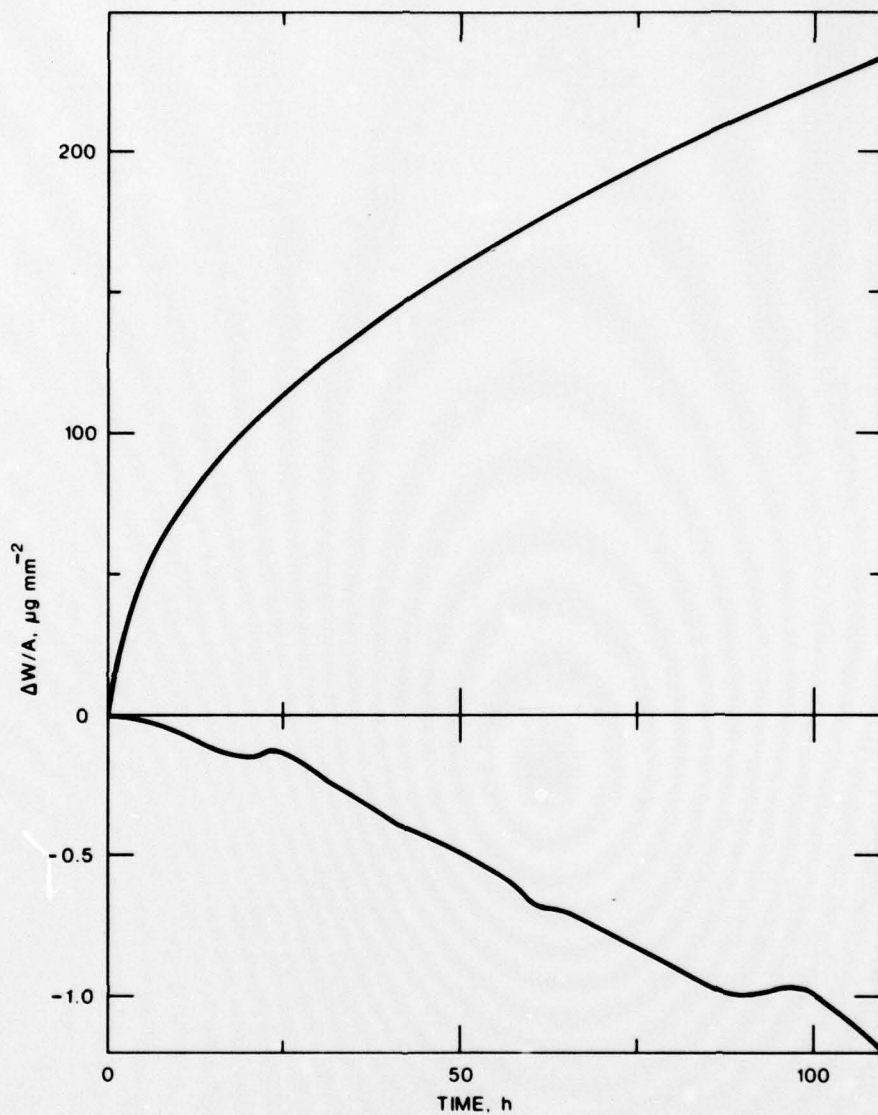


FIG. 1 - Examples of weight change curves obtained thermogravimetrically in air at 1373 K. Upper:- Oxidation of Ni-0.9Si. Lower:- Gaseous oxide formation from Pt.

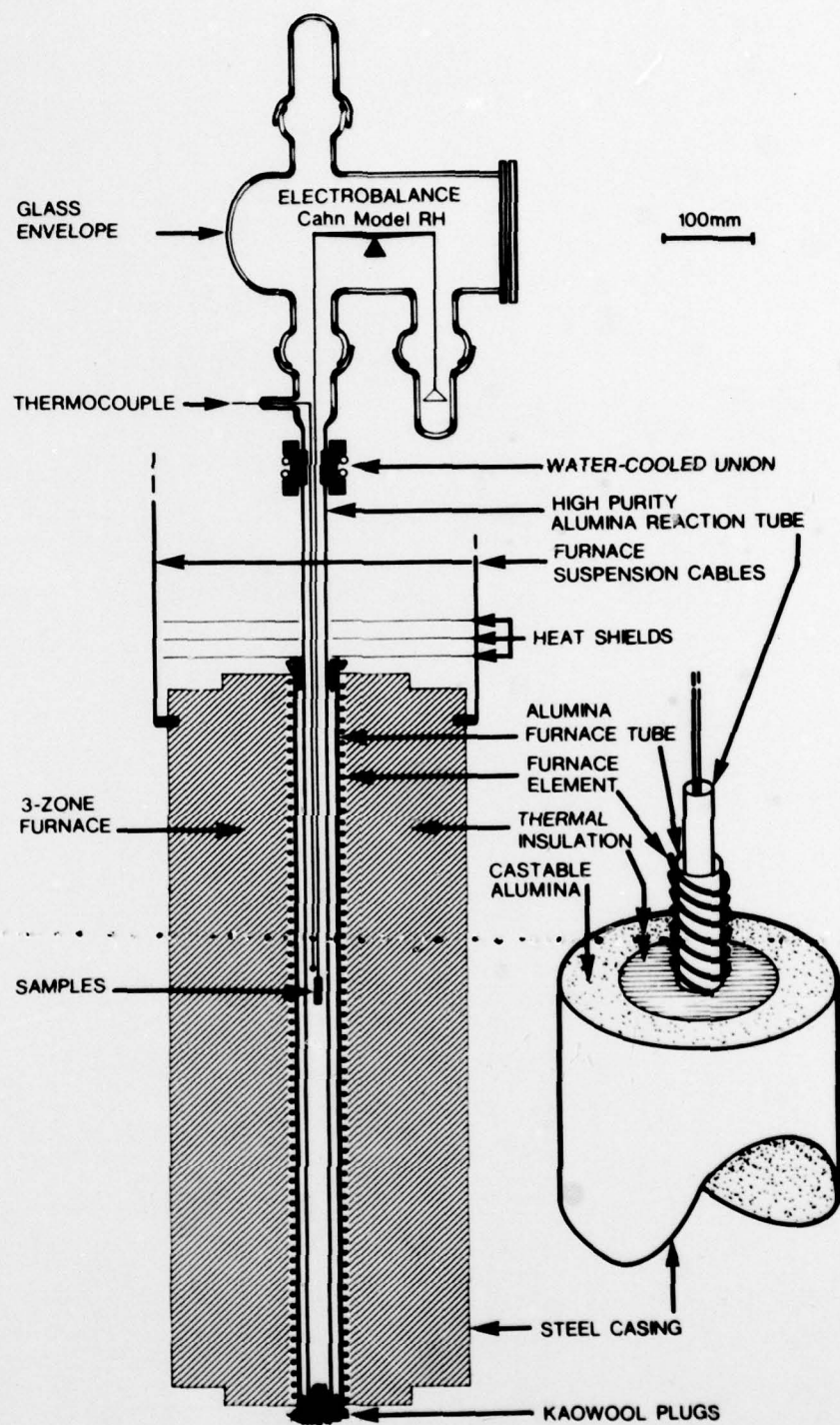


FIG. 2 - MRL thermogravimetry system.

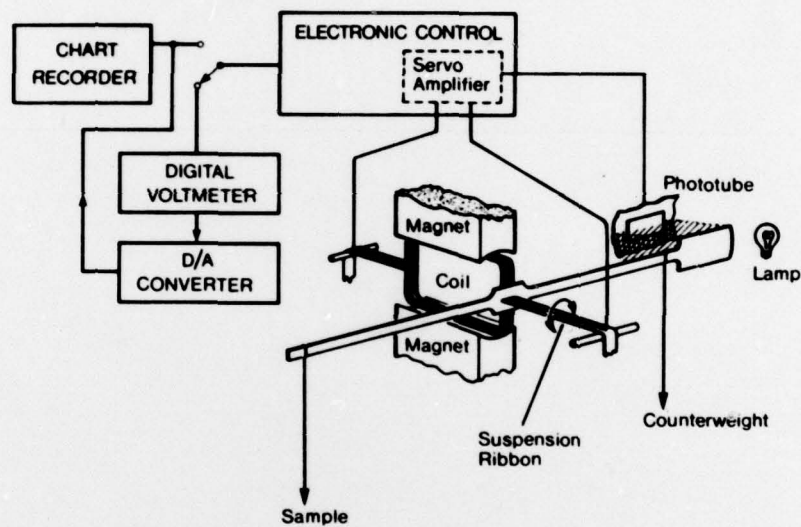


FIG. 3 - Operating principles of the Cahn RH electrobalance.

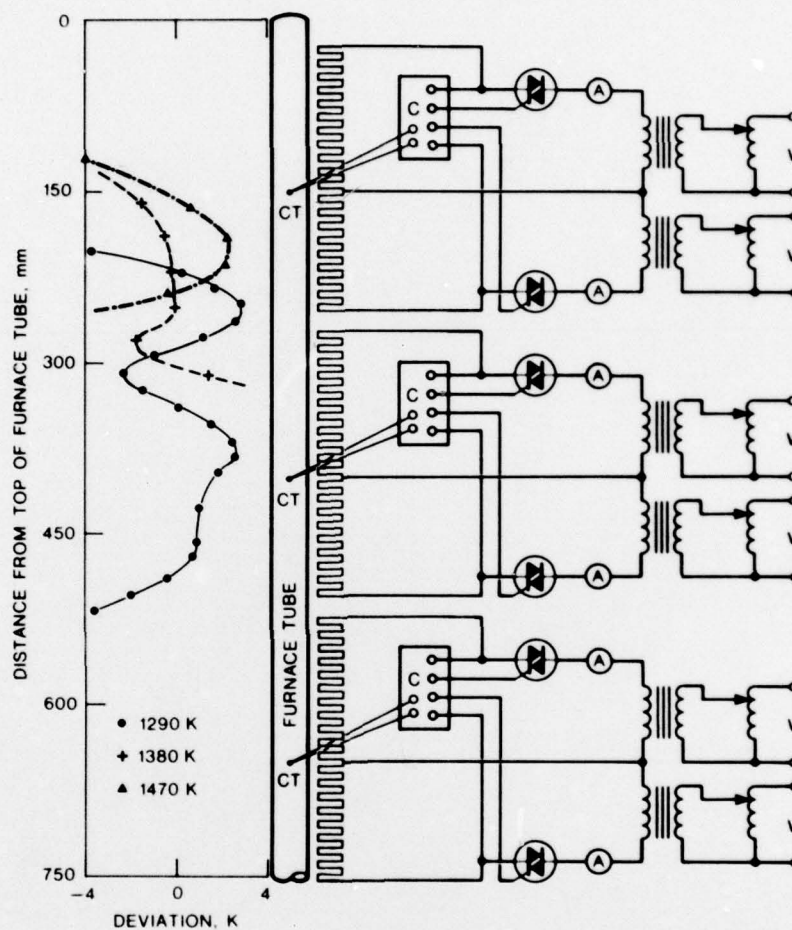


FIG. 4 - Hot-corrosion furnace power and control circuitry, and the optimum temperature gradients in the furnace tube for isothermal thermogravimetry. CT = control thermocouple, Pt-13Rh/Pt; C = temperature controller; V = variable autotransformer; A = ammeter.

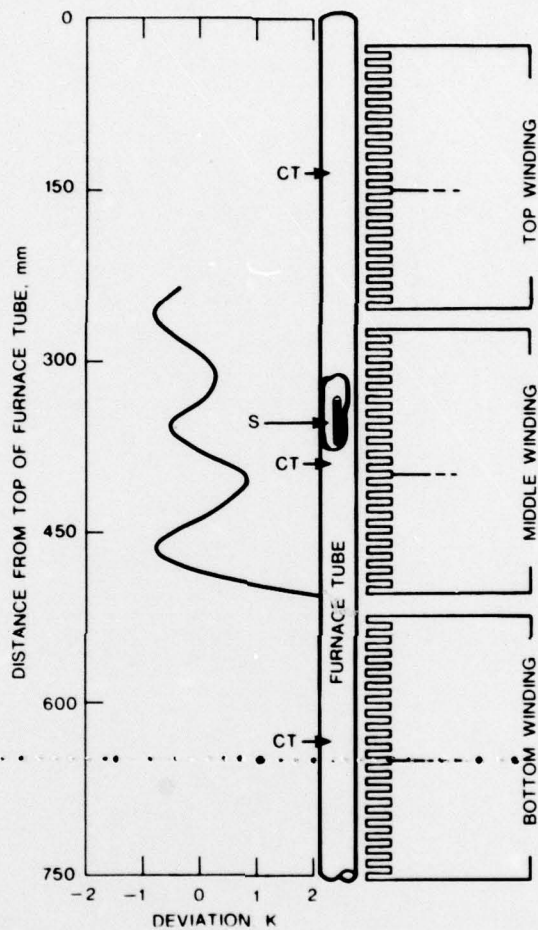


FIG. 5 - Microsil furnace element, and the optimum temperature gradient at 1373 K. CT = control thermocouple; S = thermogravimetry sample location.

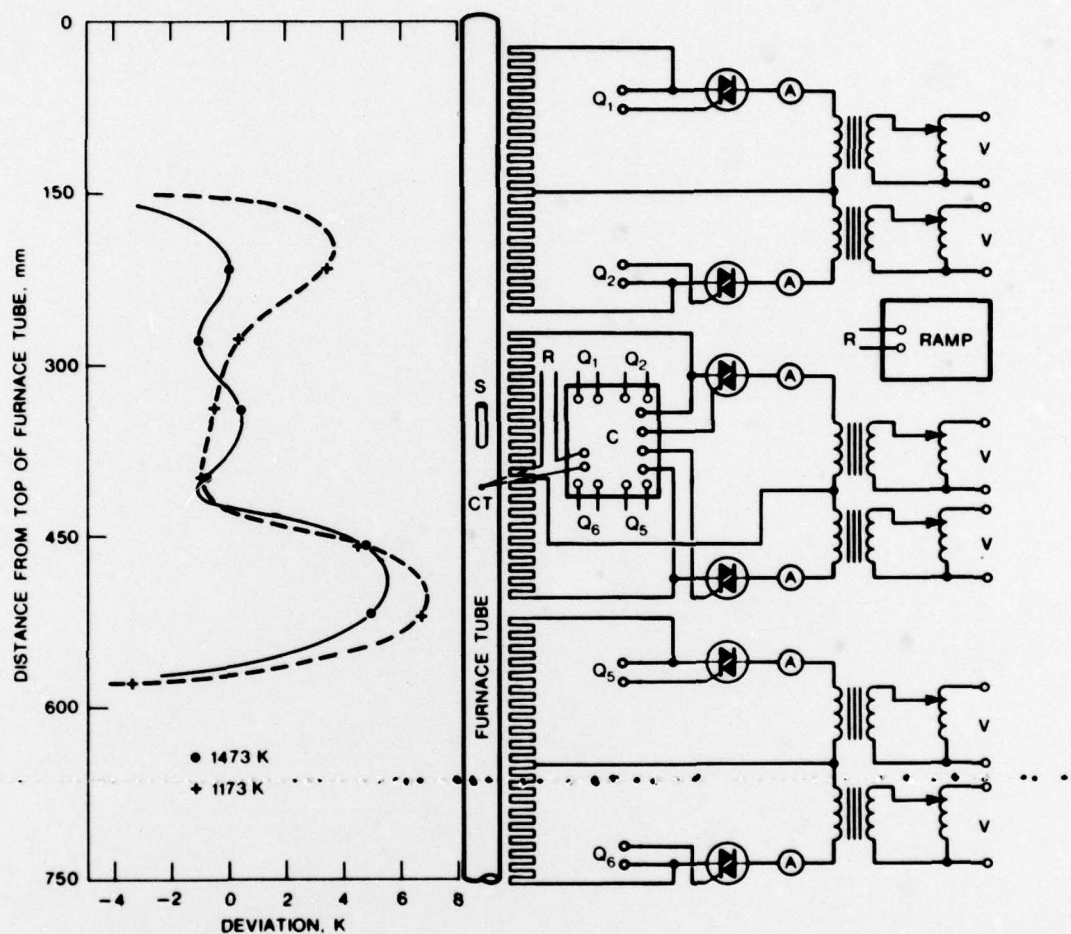


FIG. 6 - Thermogravimetry furnace with furnace-element material 'Kanthal A1', showing power- and temperature-control circuitry, and the optimum temperature gradients for isothermal thermogravimetry at 1473 and 1173 K. CT = control thermocouple, Pt-13Rh/Pt; C = temperature control, Pt-13Rh/Pt; RAMP = programmable millivolt ramp generator; V = variable autotransformer; A = ammeter; S = thermogravimetry sample location.

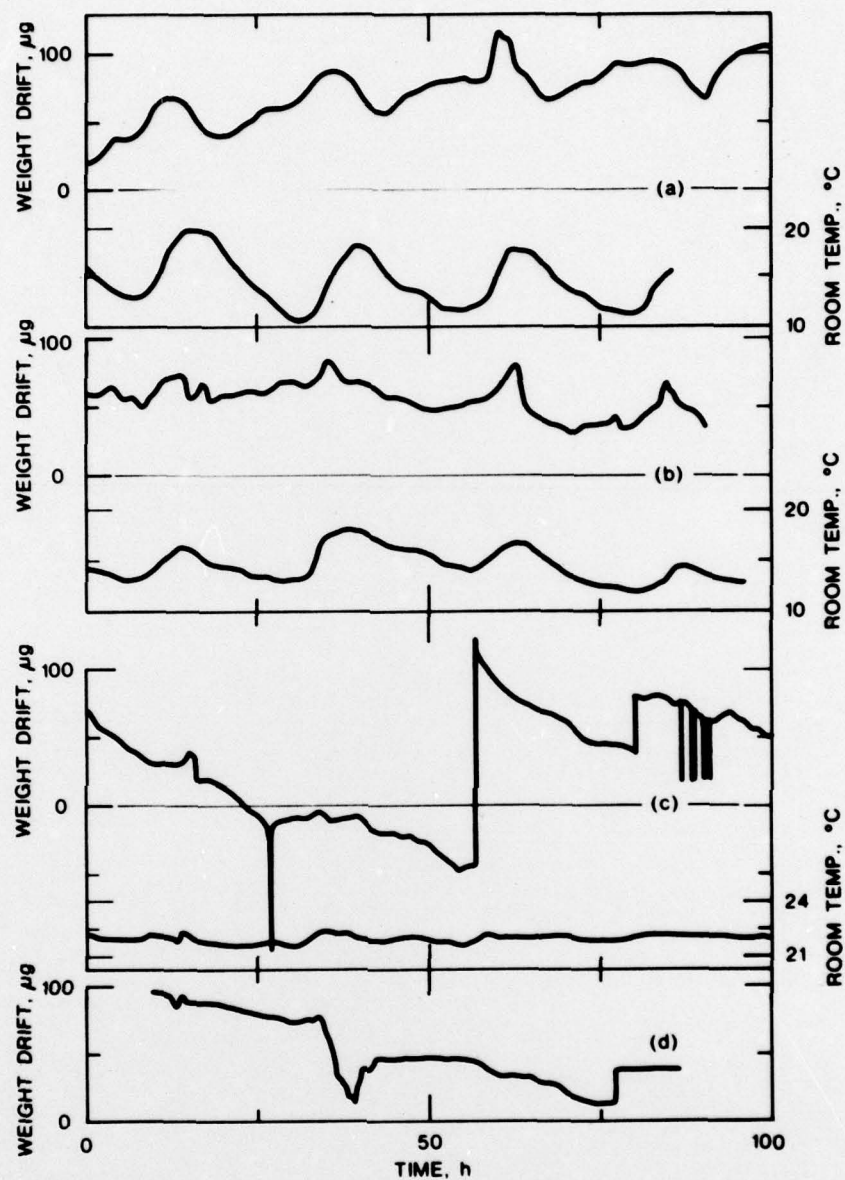


FIG. 7 - Drifts in the weight reading of the electrobalance with constant mass loads, and the simultaneous variation in room temperature; (a) prior to temperature compensation of the electrobalance output; (b) after compensation; (c) and (d) in an air-conditioned laboratory.

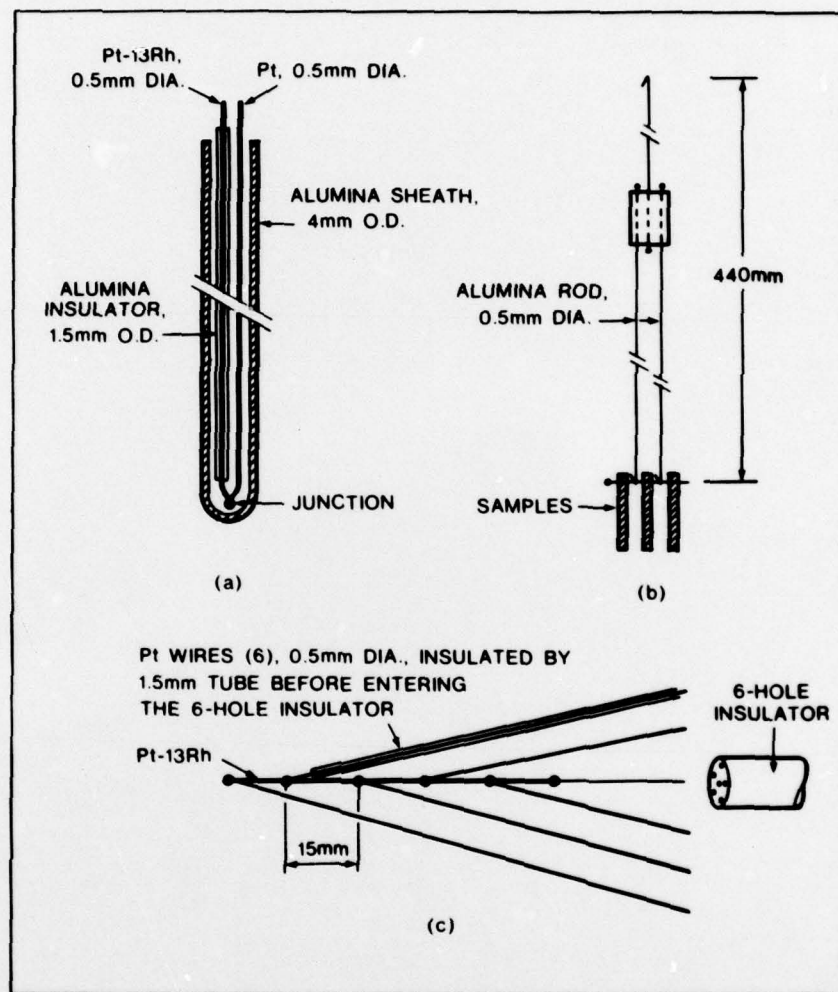


FIG. 8 - (a) Specimen thermocouple; (b) Alumina sample-suspension; (c) Six-junction differential thermopile.

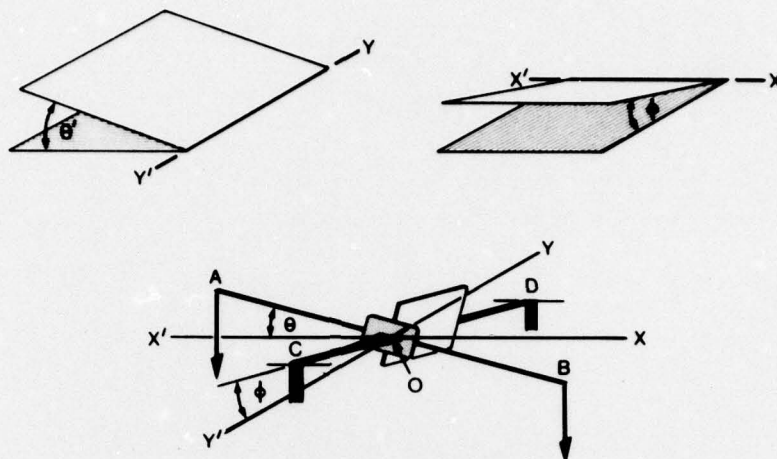


FIG. 9(a) - Definition of the angles θ , θ' and ϕ . AB represents the electrobalance beam, inclined at an angle θ to the horizontal plane defined by the lines XOX' and YOY' . C and D are the support points for the beam and coil assembly (see Fig. 3).

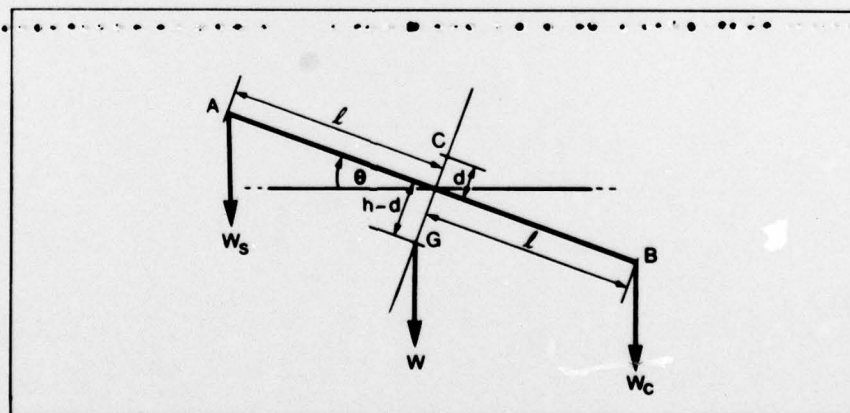


FIG. 9(b) - Force diagram for the electrobalance beam inclined at an angle θ to the horizontal. The electromagnetic torque is not shown.

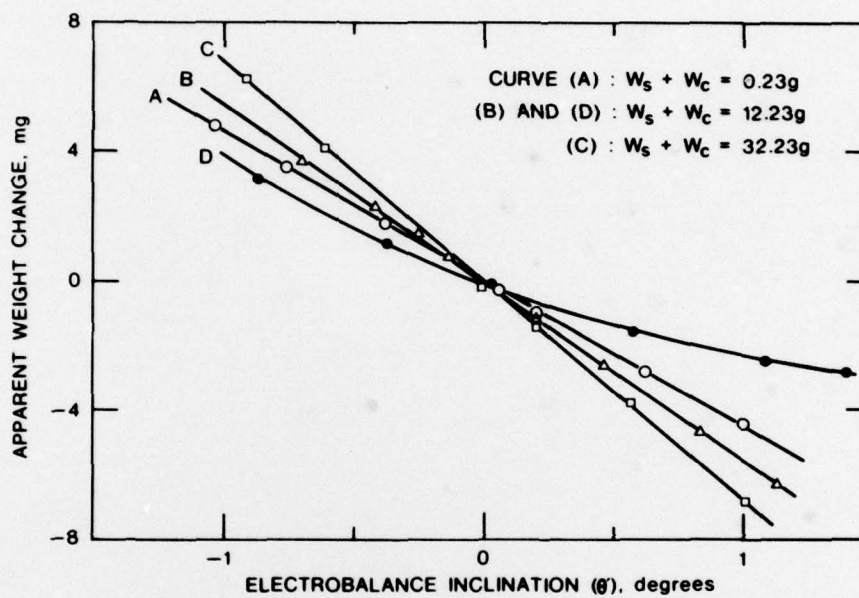


FIG. 10 - Changes in electrobalance output as a function of inclination angle θ' . $W_s - W_c = 0.00$ g for A, B and C, and -4.50 g for D.

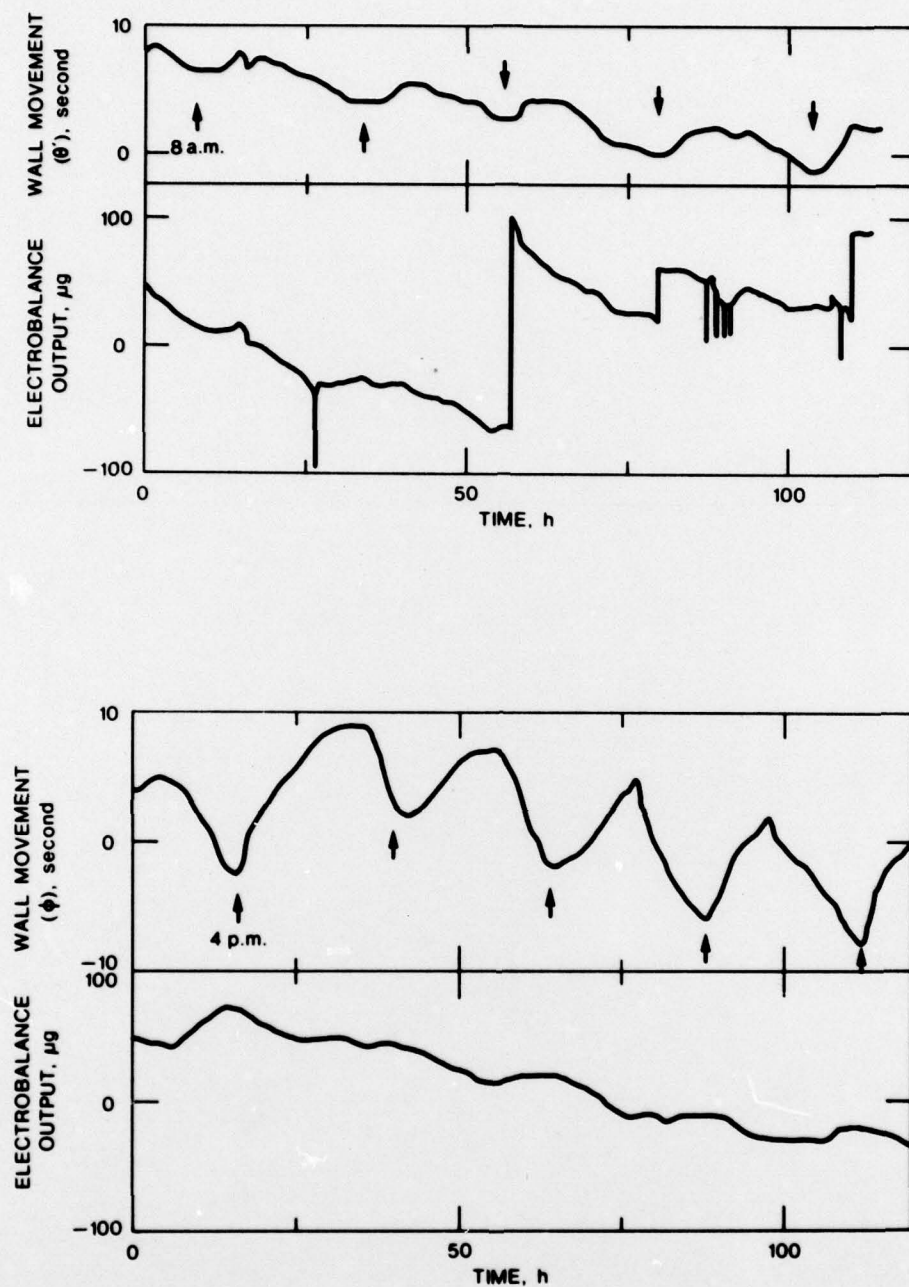


FIG. 11 - Angular movement of the wall on which the electrobalance is mounted, and the simultaneous output of the electrobalance. Upper:- variation in θ' ; lower:- variation in ϕ .
 † denotes 8 a.m., or 4 p.m.

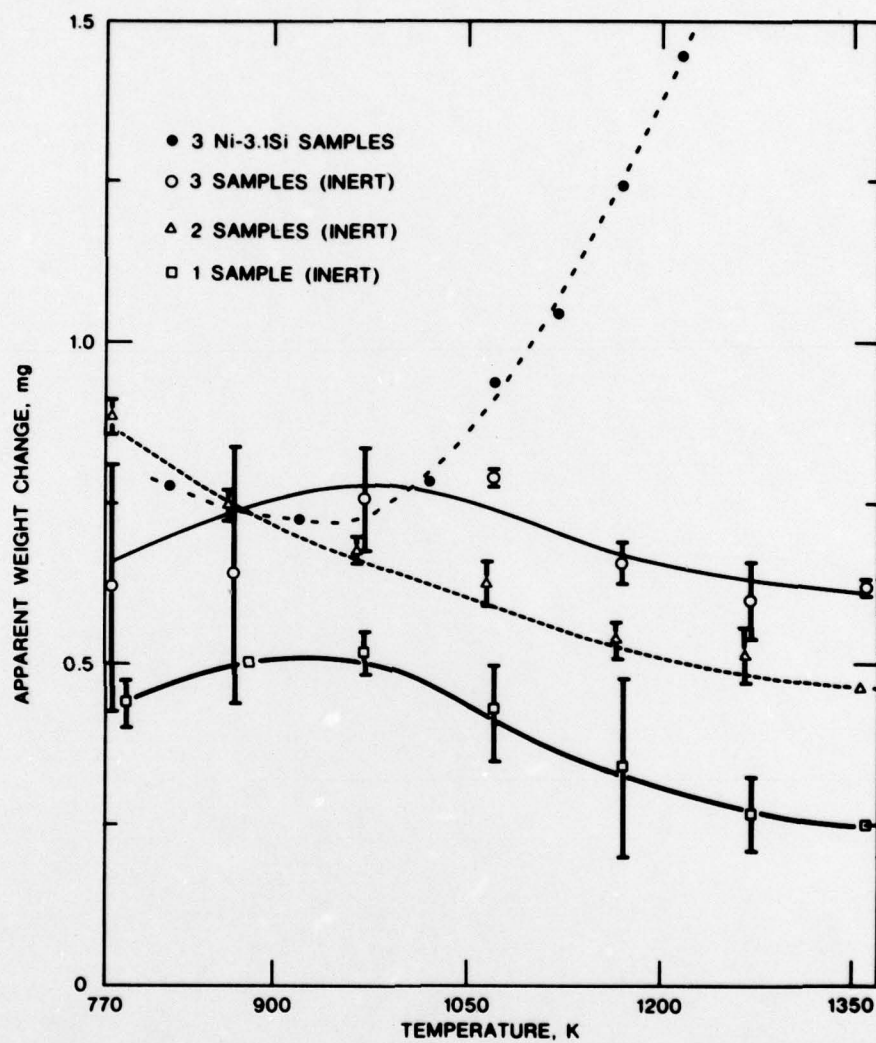


FIG. 12 - Change in apparent weight of inert alumina samples and of Ni-3.1Si alloy samples during rapid heating in air to 1370 K. Samples were cylindrical, 3 mm diam. and 35 mm long.

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National Research Council, Canada (Attention: Division of
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