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The history and development of thermogravimetry

VII. The influence of the French school on the development of thermogravimetry

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1. Introduction

The first indication of an interest in thermogravimetry (TG) by a French worker appeared in 1912 when Georges Urbain [1][1] commented on the shortcomings of using an ordinary analytical balance for studying materials which decompose at a perceptible rate with the evolution of a gas. Accordingly the weights of the balance were replaced by a magnetised needle suspended vertically from one end of the balance beam into a solenoid. The balance pan on the opposite end of the beam was suspended in the centre of an electric furnace whose temperature could be regulated and measured with the aid of a sensitive thermocouple. The balance case was made airtight and sufficiently robust to support a vacuum and appropriate reagents were placed in the case capable of absorbing evolved gases. Using this apparatus Urbain and co-workers studied the efflorescence of hydrates in a dry atmosphere [2,3], but the concepts of operating at a continuously varying temperature and absorbing the evolved gases were not pursued because, accordingly to Clement Duval, “the results depended too much on the heating conditions” [4]. Although little became of Urbain’s efforts, it was, nevertheless, the first reported occasion that an attempt to use TG was made in France. Sadly, his original apparatus was vandalised during the German occupation of France in World War II [4].

No further papers in TG occurred in France until 1923 when Marcel Guichard [5] reported, briefly, on a “kinematic method” for determining the states of hydration of compounds based on determining the mass changes as a function of regularly increasing temperature. This brief note marked the beginning of one of the most influential contributions by a single worker to the development of TG. In a subsequent paper [6], in propounding the technique of dehydration at a regularly increasing temperature Guichard presents, for the first time, formalised mass loss curves (Figs. 1 and 2). Thus, in Fig. 1 plateau A is equivalent to the mass of the hydrate and plateau B corresponds to the anhydrous material, unless the substance has several hydrates, in which case B corresponds to a lower hydrate. This lower hydrate acquires an appreciable vapour pressure and the curve tends towards a third plateau C, which represents a new hydrate (or the anhydrous material). In Fig. 2 Guichard explains that this type of mass loss curve will be obtained if the material has no definite hydrates. Guichard thus con-

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[1] In order to avoid disrupting the narrative, biographical notes of key workers in TG are given in Appendix A.

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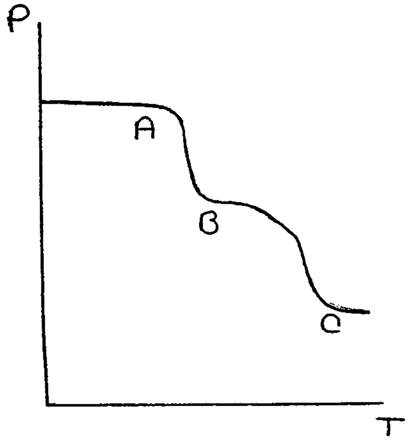

Fig. 1. Formalized weight loss curve.

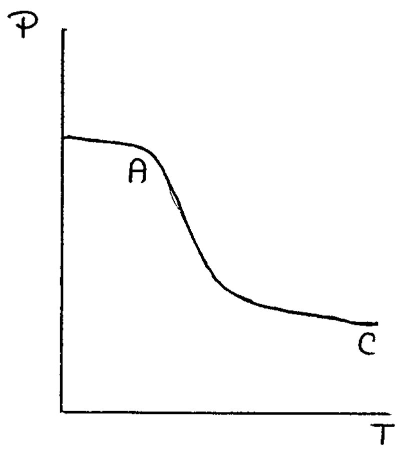

Fig. 2. Formalized weight loss curve (after Guichard [6]).

cludes that the classical method of dehydration at constant temperature is inadvisable if carried out to the stage of a constant mass at each temperature, since it is not always easy to decide whether a definite hydrate has been formed or whether, under the given operating conditions, the material merely loses water with difficulty. On the other hand, with the proposed method of dehydration at a regularly increasing temperature, a plateau is formed only when there is a definite combination of water and solid. Guichard then verifies these conclusions using the dehydration of $Na_2HPO_4 \cdot 12H_2O$ as an example of a material possessing well defined lower hydrates and Al_2O_3aq as a material having no intermediate hydrates [6].

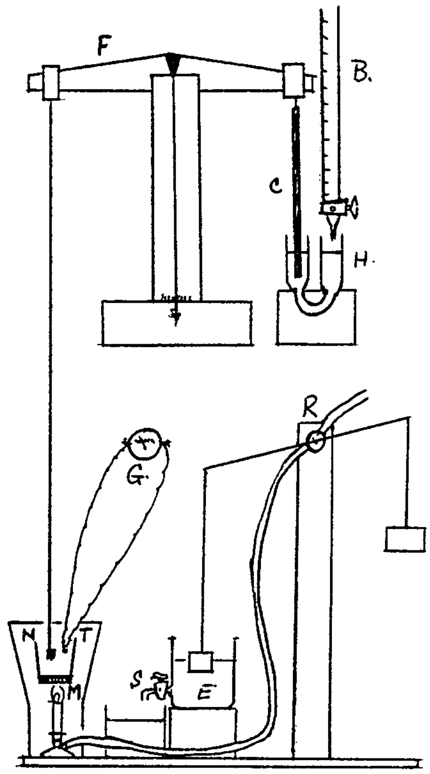

Fig. 3. Guichard's first thermobalance [7].

Details of Guichard's apparatus, together with a line drawing (Fig. 3) were given in a subsequent publication [7]. The furnace consists of a metal shield in which is positioned a metal crucible (M) containing a layer of asbestos at the bottom. A regular increase in temperature is achieved by means of a gas burner regulated by a ball-cock (R) activated by a float, supported on water (E) which, in turn, floats at a slow and regular rate through the stop-cock (S). The temperature is continuously recorded by means of the thermocouple (T). An initial trial run determines the adjustment of the stop-cock (S) necessary to achieve the required heating rate. The hydrostatic compensation balance was constructed from an ordinary balance modified as follows: from one end of the balance beam (F) was suspended the small crucible (N) containing the sample. This crucible is positioned inside the metal crucible (M) and the suspending wire passes through a small hole in an asbestos lid. The thermocouple is positioned to one side of the small crucible (N), the thermocouple and the crucible remaining stationary during the experiment. At the other end of the balance beam a cylindrical rod (C) is partially immersed in oil in a U-tube (H). Progressive addition of oil from the burette (B) compensates for the upward movement of the cylindrical rod, which occurs when the material looses mass on heating. Providing the balance is maintained at zero, the volume of the oil added is exactly proportional to the mass variations. Guichard claimed that sensitivity and reproducibility were better than 1/2 mg. Above 400°C there were always slight oscillations due to turbulence of gases in the furnace.

The severe limitation of the above apparatus, i.e. only being able to detect mass losses was appreciated and attended to by Guichard in a subsequent publication [8] in which a modification to the hydrostatic compensation balance was incorporated. In addition, the gas burner assembly was replaced by an electric furnace and a facility was provided for carrying out experiments in a flowing gas atmosphere.

Several workers in France were inspired by Guichard's preliminary work to carry out experiments on a variety of materials, for example, hydrated calcium oxalate [9], platinum complexes [10], hydrated calcium aluminates [11] and manganese salts [12]. The results obtained by these workers caused Guichard to comment on the effect that procedural variables had on the shape of the TG curve [13,14] to improve further his apparatus by incorporating a mercury regulator which achieved more accurate temperature control [15]. This also prompted him to use TG to study analytical precipitates [15], a course of action which subsequently inspired Duval to carry out his monumental work on this subject [16]. When new techniques are introduced or substantially developed, a review prepared by the originator or the developer is invariably of use, either to himself or subsequent workers in the field. Guichard's penultimate paper was such a review [17], whereas in his final communication [18] mention is made of using a "chainomatic" balance — but with no details.

Several of Guichard's students were concerned with the practical and theoretical applications of TG. Outstanding among these was Pierre Vallet, who made many fundamental contributions to both the practical and theoretical innovations of TG. His first contribution was in platinum metal chemistry, in which he studied the decomposition of $(NH_4)_2PtCl_6$ [19], followed by a further publication on the decomposition of K_2PtCl_6 [20]. In these experiments, Vallet used a modified Guichard apparatus employing an electric furnace regulated by a rheostat and an ammeter. Realising the necessity of very slow heating rates, he constructed a liquid rheostat. This consisted of a glass cylinder 10 cm in diameter and 50 cm high containing copper sulphate solution. The electrodes were two thin circular copper discs, one fixed inside the base of the cylinder and the other near the top, movable in a vertical plane. current was transmitted to the electrodes via thick copper wire, that which was connected to the fixed, lower, electrode was glass covered to obviate accidental contact to the movable electrode. The copper wire connected to the movable electrode was attached to a thin card which passed over a pulley and connected to a float placed in a second cylinder containing water. The displacement of the float and thus the variation of the distance between the electrodes was achieved by dropwise addition of water to the second cylinder. Vallet subsequently published further modifications to Guichard's apparatus including simultaneous photographic recording of mass/time and temperature/time curves [21,22] and slower heating rates with improved photographic recording [23].

Having considerably modified Guichard's original apparatus, Vallet discussed in some detail the effect of procedural variables on the shape of the TG curve [24]. Some 25 years later other investigators who were aware of his work using vastly superior equipment, arrived at very similar conclusions and his general classification of procedural variables were subsequently followed by other workers [25,26]. Although it is considered unnecessary to report at length on this subject, one example will illustrate Vallet's observations. He investigated the thermal decomposition of $CuSO_4 \cdot 5H_2O$ and found that the TG curves obtained were dependent upon the heating rate. Only at the slowest heating rate (30°C/h) could the formation of $CuSO_4 \cdot 3H_2O$ as an intermediate be distinguished.

Probably the most extensive use of TG in theoretical chemistry is in the evaluation of kinetic parameters. In spite of the profusion of literature on this subject over the years it is not widely appreciated that the theory covering the kinetics of decomposition and the concept of activation energy as applied to rising temperature experiments was set out quite clearly by Vallet as early as 1935 [27].

There is no question that Vallet's contributions to the development of TG were quite outstanding but it is impossible to say whether any of his contemporaries were capable of similar studies, although Duval seemed to doubt it [28]. Nevertheless, mention must be made of contemporary workers who, at the time, also made useful contributions to the development of TG; for example, Dubois [29,30] studied the decomposition of manganese compounds, Longchambon studied the dehydration of minerals [31], Selva the decomposition of various phosphates and arsenates [32], and Shreiber [33], carried out a comprehensive research programme on the decomposition of dithionates.

In 1912, when Urbain carried out his tentative experiments, the outlook did not seem very favourable for any outstanding contributions to come from France on the development of TG. Yet, some 10 years or so later, this was to change completely with the entrance into the field of TG by Guichard and his co-workers. It is, surely undeniable, that the subsequent publications place France at the forefront of the early development of TG.

Appendix A.

Georges Urbain was born in Paris on 12 April 1872, the son of a Professor of Chemistry at l'Ecole Lavoisier et de Chimie Industrielle de la Ville de Paris and graduated, as top student, in 1894. He obtained his D.Sc. in 1899 with a thesis on the Rare Earth (RE) elements. From 1899 to 1904 he worked in industry as head of the laboratories of la Compagnie Generale d Electricitie but his true vocation was in pure science, and after 1904 he taught, initially at l'Ecole de Physique de la Chimie and latterly at the Sorbonne, where he became Professor of Chemistry in 1908. His research interests lay mainly in the field of RE chemistry and he is probably best known for his discovery of lutetium and for his unsuccessful attempts at isolating another RE metal which he hoped to call Celtium. In addition to his duties at the Sorbonne he also taught at l'Ecole Centrale des Arts et Manufactures and was Director of l'Institute de Chimie Appliquee. During World War I Urbain was occupied with devising formulations for producing smoke screens. In 1921 he was elected to l'Academie des Sciences and was also a Commander of the Legion of Honour.

In his leisure time he enjoyed playing and listening to music and was also a particularly proficient sculptor. He died, suddenly, on 5 November 1938.

Marcel Guichard was born on 17 December 1873 at Charenton (Seine), the son of a pharmacist. He became a Licencie es Science in 1893, a Doctor of Physical Sciences in 1900 and obtained his pharmacist's Diploma (1st Class) in 1901. He initially worked in the laboratory of Henri Moissan and learned from him an outstanding practical ability. In 1909, he was appointed a senior lecturer at the Sorbonne and worked for the next 10 years or so in Le Chatelier's laboratory.

During World War I he was recruited into the army for 2 years and together with several colleagues was given the task of attempting to synthesise ammonia by high pressure catalysis. This work was very successful and gained for Guichard a high reputation. After his demobilisation in 1919 he was elected to the Chair of Analysis and Chemical Measurement at the Sorbonne. He initiated many research projects, his two most successful being his work on the determination of the atomic weight of iodine and TG.

In addition to his teaching and research at the Sorbonne, he was, in 1925, put in charge of the laboratories at the Mint — a post traditionally occupied by an outstanding French chemist. However, in 1932, the pressures of work at the Sorbonne were so great that he was, reluctantly, forced to resign from this post. Guichard was particularly proud of the fact that he and Le Chatelier were responsible for introducing the concept of tutorials at the Sorbonne.

Although he retired in 1940, he continued to direct his research school and several of his students were later to occupy important posts in research and industry. He died in his 87th year on 7 February 1960.

Pierre Vallet was born, in Paris, on 11 November 1906. After primary and secondary school, he entered the Sorbonne in 1926 and was awarded the Licence ès Sciences physiques in 1927. He remained until 1939 except for a short break between 1928 and 1929, when he was enlisted in the military service. During this period at the Sorbonne he commenced his fruitful relationship with Guichard and in 1936 was awarded the D.Sc. in recognition of his work in the field of TG.

In September 1939, he was called up into the army and taken a Prisoner-of-War in June 1940. During this internment he was elected, by his junior Officers, "University Rector" and carried out a limited amount of theoretical studies until his release in August 1944.

Between 1944 and 1958 Vallet had a succession of teaching posts in various Lycees and also carried out research on behalf of C.N.R.S. and the Institut de Recherches de la Siderurgie. In 1959 he was appointed Lecturer in the Faculty of Science at Rennes University and became Professor in 1961.

On his retirement in 1969 he lived in Paris and continued to take an active interest in thermal analysis until, in later years, failing health necessitated his moving into a nursing home in Paris where he died in 1995.

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