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THE USE OF THE THERMOBALANCE IN ANALYTICAL CHEMISTRY

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BY

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THE USE OF THE THERMOBALANCE
IN ANALYTICAL CHEMISTRY
Examples of Application (*)

by

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The Chevenard-type thermobalance is described. Methods are given for determining the percentage of goethite in iron ores and brucite in magnesium-bearing rocks. The same methods with slight variations may be used for other kinds of analyses. The accuracy and the limitations of the apparatus are discussed.

INTRODUCTION

The methods of analytical chemistry are now progressing through the rapid development of modern techniques based on physical principles such as polarography, X-Ray fluorescence and absorption, spectroscopy, etc.

The regular gravimetric methods, nevertheless, should not be neglected. They are still very useful and in a great number of cases cannot be easily replaced by other methods. However, while the gravimetric methods of analysis are brought up to date with time, their general feature is not substantially changed. A new instrument, the thermobalance, which was put on the market a few years ago, has been designed to improve substantially the existing gravimetric methods of analysis, and to determine new ones. This apparatus allows the analyst to see what is happening to his samples when heated and permits him to find out the effect of the other constituents on certain reactions. Also, certain types of analysis which were almost impossible to do by conventional methods can now be done more easily, more accurately and in a shorter time.

The principle on which the thermobalance method or the continuous weighing method is based is quite simple. Most of the known substances that decompose with weight change when heated happen to do so at a characteristic temperature which practically varies very little. If the rate of heating is not too fast, the weight of a sample will change very rapidly at the characteristic temperature of transformation while it will stay constant outside that range of temperature.

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The thermobalance is the apparatus that registers these changes of weight as a function of the temperature.

DESCRIPTION OF THE CHEVENARD THERMOBALANCE

The Chevenard-type thermobalance which will be described here is essentially composed of a balance, a furnace and a photographic recorder (Fig. 1). The beam of the balance is supported by four very fine tungsten wires in order to minimize friction; a vertical fused silica rod is suspended at one end of the beam and penetrates into the furnace where it holds a crucible and the sample. At the other end of the beam a curved platinum mirror reflects a beam of light coming from a fixed light point source. That beam of light is focussed on a photographic paper which is wrapped around a motor-driven drum. The slight variations in the equilibrium position of the balance are thus recorded on the photographic paper. These variations can be increased or decreased at will by changing the position of the counterweight C_2 which changes the center of gravity of the balance and evidently influences the sensitivity. The best sensitivity that can be obtained is in the order of 1/2 mg per mm. as read on the photographic paper.

The temperature of the furnace is increased with a rate of heating of 5°C/min. up to 1000°C by means of an electromechanical program controller which has proven to be very efficient although of a very simple and rough construction. The temperature of the sample is registered on a Brown strip chart potentiometer, and fiducial marks are automatically registered at intervals of two minutes simultaneously on the photographic paper and on the temperature chart. This allows for complete correlation between temperature and change of weight. This temperature recording is not absolutely necessary but is a good addition to the apparatus.

APPLICATION TO THE DETERMINATION OF GOETHITE

These curves indicating change of weight as a function of the temperature, called thermograms, can be used for quantitative analysis in a number of reactions as pointed out by Duval in the September 1951 issue of the "Analytical Chemistry". To illustrate the use of the method, two examples of determinations will be described that have been worked out in the Quebec Department of Mines Laboratories and which are not of the type of analysis considered by Duval. The problem is to determine the amount of a mineral in a sample where the constituents of the mineral are also found in the sample.

The first case is that of the determination of goethite in iron ores. Since goethite is a hydrated iron oxide, its chemical quantitative determination is complicated by the presence of other iron-bearing minerals such as hematite, magnetite, siderite, or hydrated minerals such as kaolinite. But the continuous weighing method offers a simple way of carrying out the analysis. Goethite is known to decompose into hematite and water at about 375°C. (Fig. 2). The reaction starts slowly at about 100°C. below this temperature and ends at about 100° above it. In the simple case where no other reactions interfere, the amount of goethite will be easily calculated by measuring the difference of height of the two portions of the curve before and after the reaction. This is converted in percentage of goethite by the formula:

$$\% \text{ Goethite} = \frac{hs + k(T_2 - T_1)}{p} \times 987$$

where h is the difference of height measured on the curve.

s the sensitivity of the balance.

$k(T_2-T_1)$ is the correction factor, which will be discussed later.

p the initial weight of the sample.

987 a conversion factor $= \frac{\text{weight } Fe_2O_3 \cdot H_2O}{\text{weight } H_2O} \times 100$

Not all goethite analysis are as simple as this. Most of the time other reactions, such as the decomposition of kaolinite, interfere with the beginning or the end of the goethite transformation which prevents obtaining an accurate measure of the value of "h" used in the previous equation. However, it has been found that the first and last portion of the curve of the dehydration of goethite are quite straight. When these lines are extended to meet the vertical through the middle of the transformation, then the distance between these intersections is related to the percentage of goethite. The observations then lead to the formula (without thermobalance):-

$$\% \text{ Goethite} = \frac{1081\ sh' + 2500}{p}$$

where s sensitivity in mg/mm.

h' height determined as above.

p initial weight of sample in mg.

This last method has been checked on 28 synthetic mixtures of goethite with quartz, hematite, kaolinite, siderite and calcite; in 25 cases, that is in 90 per cent of the cases, the divergence was less than 2 per cent.

APPLICATION TO THE DETERMINATION OF BRUCITE

The case of brucite, magnesium hydroxide, is even more acute than that of goethite. Brucite is frequently associated with serpentine, hydrated magnesium silicate, dolomite, calcium and magnesium carbonate, etc., which are all magnesium-bearing minerals and which, as such, prevent the accurate determination of brucite by regular analytical methods. When no serpentine or other interfering mineral is present, the analysis can be carried out easily by the first straightforward method described for the analysis of goethite. Serpentine is a serious interfering element in the determination of brucite on account of the wide interval of temperatures where its decomposition occurs with much overlapping on that of brucite. However, regular samples usually do not contain more than 10 per cent serpentine and in that case a simple method can be divided for samples containing any percentage of brucite. Two points can be determined on the thermogram (Fig. 3) by producing the two rectilinear parts of the curve before and after the brucite transformation and drawing the tangent to the steepest part of the transformation curve. The vertical distance between these two points represents a loss of weight which, if multiplied by an experimental factor which varies a little with percentage for low brucite concentrations, will give the brucite percentage within an accuracy of 1 per cent. Of course, if large errors can be tolerated, greater amounts of interfering serpentine are permissible. In this last case, the accuracy could also be kept high by introducing a correction factor which would be dependent on the amount of serpentine, but this has not been investigated as yet.

At this point, other cases could be added which would be particularly difficult to handle by regular analytical methods. For example, the determination of calcite in a mixture of calcite ($CaCO_3$) and dolomite ($CaCO_3.MgCO_3$); both contain Ca and CO_2. Also, the determination of the amounts of different sub-oxides of the same metal such as in a mixture of FeO, Fe_3O_4 and Fe_2O_3. Such determinations can be easily done by the Thermobalance method.

LIMITATIONS OF THE THERMOBALANCE

The interference effects we have found in the examples described suggest that I say a few words about the limitations of the Chevenard-type Thermobalance.

First of all, it should be remembered that only the substances that change weight by heating can be analysed. Others can be analysed only if they can be previously transformed into suitable compounds that will also lose or gain weight by heating. An example of this is the case of the determination of free CaO in a mixture. No evidence of CaO will be found on a thermogram, but if an excess of water is added to the sample before heating, the calcium oxide will be transformed into the hydroxide which will now show a loss of weight at about 600°C.

The shape of the thermogram for a single compound is also important. Dehydration and decarbonatation usually happen in a narrow interval of temperature and these reactions are suitable for analysis; on the other hand, oxidation curves are frequently complex and sometimes can scarcely be of any use even for semi-quantitative determinations. Moreover, they tend to mask or interfere with other reactions which have been chosen for analysis. This effect can be overcome, however, by the use of a special adapter which permits operating in controlled gas atmospheres. This adapter could also be used for minimizing interferences from dehydration or decarbonatation by working in atmospheres of H_2O vapour, CO_2 or N_2 gas.

All the above mentioned limitations come from the nature of the reactions which are taking place and which are not easy to control. There are also other limitations arising from the apparatus and the method. The Chevenard-type thermobalance made by the "Société Anonyme Commentry-Fourchambault" would theoretically permit a maximum accuracy in the order of 0.2 mg. This maximum accuracy is rarely attained, however, on account of two temperature effects: convection currents and variation of the density of the air in the furnace.

It is well known that inside an open container, the higher the temperature the lower is the density of the air. If it is assumed that the gas law holds in first approximation for temperatures up to 1000°C, it can be figured that the result will be an apparent increase of weight given approximately by the formula:

$$\Delta W_1 = Vd \left(1-\frac{273}{T}\right)$$

where ΔW_1 apparent weight increase.

V volume of sample, crucible and holder.

d density of air at 25°C.

T temperature in °K.

It should be borne in mind that this equation is only an approximation: first, from the fact that the gas law is not exactly obeyed, specially over such a range of temperatures, and, secondly, from the fact that the value of V cannot be determined accurately, because the silica rod which holds the crucible is in a region where the temperature is not constant.

The second temperature effect is the formation of convection currents which are caused by the unevenness of the heating in the furnace. The warmer air tends to go up at the surface of the furnace core and vortices are produced which exert a downward pressure on the crucible and so cause another apparent increase of weight.

The effect is small at low temperatures but increases rapidly at higher temperatures; it apparently follows the equation:

$$\Delta W_2 - Ae^{bT}$$

where ΔW_2 - apparent weight increase.

T - temperature in °K.

In an experiment that was carried out with an empty crucible, the volume of the holder and the crucible was estimated to be 3.0 cm^3. In that case, the theoretical weight increase can be made to correspond with the observation if the coefficients A and b are given the respective values of 0,14 and 2.6×10^{-3}.

The theoretical and observed curves are shown in Figure 4. It follows that in the general case, when a sample is run, the correction factor should then be given by the formula:

$$\Delta W = 1.3\ (3+V) \left(1-\frac{273}{T}\right) + 0.14e^{2.6 \times 10^{-3}T}.$$

where ΔW apparent weight increase in mg.
V volume of sample only in cm^3.
T temperature in °K.

For large temperature intervals, this factor is in the order of 6 to 8 mg. and cannot be estimated with an accuracy better than 0.5 mg., which limits the total accuracy of the method. For smaller temperature intervals, the expected accuracy is evidently higher.

Also, if time is not an important factor, the accuracy can still be made higher by using slower heating rates. The experimental conditions then correspond to better equilibrium conditions and the curves should show less interferences and more angular shapes (Fig. 5). This can be observed by comparing two thermograms of brucite, for example, those made at rates of heating of 2½ and 5 degrees centigrade per minute. It is noted that the interval of temperature where the reaction proceeds is narrowed by using slower heating rates; although the heating rates in this case differ only by a factor of two, the resolution is much better.

CONCLUSION

It follows from the above that the thermobalance is a very versatile instrument. The mention of the many other applications of the thermobalance in research is not within the scope of this paper. Although its applications in the field of analytical chemistry is only a limited part of all its possibilities, it should not be overlooked.

The literature is not very abundant on this matter and most of the publications deal with research on transformations in minerals. For applications more appropriate to the field of analytical chemistry, the reader is referred to the papers of Clement Duval. Numerous examples of thermograms of compounds are given and interpreted and some are suggested for use in quantitative analysis. The use of these curves, of course, will depend on the particular details of the analysis that has to be done. This is left to the ability of the analyst.

The writers wish to express their sincere thanks to Dr. A.O. Dufresne, Deputy Minister of Mines, who made this paper possible and to Dr. Maurice Archambault, Director of the Laboratories Branch, for his kind cooperation.

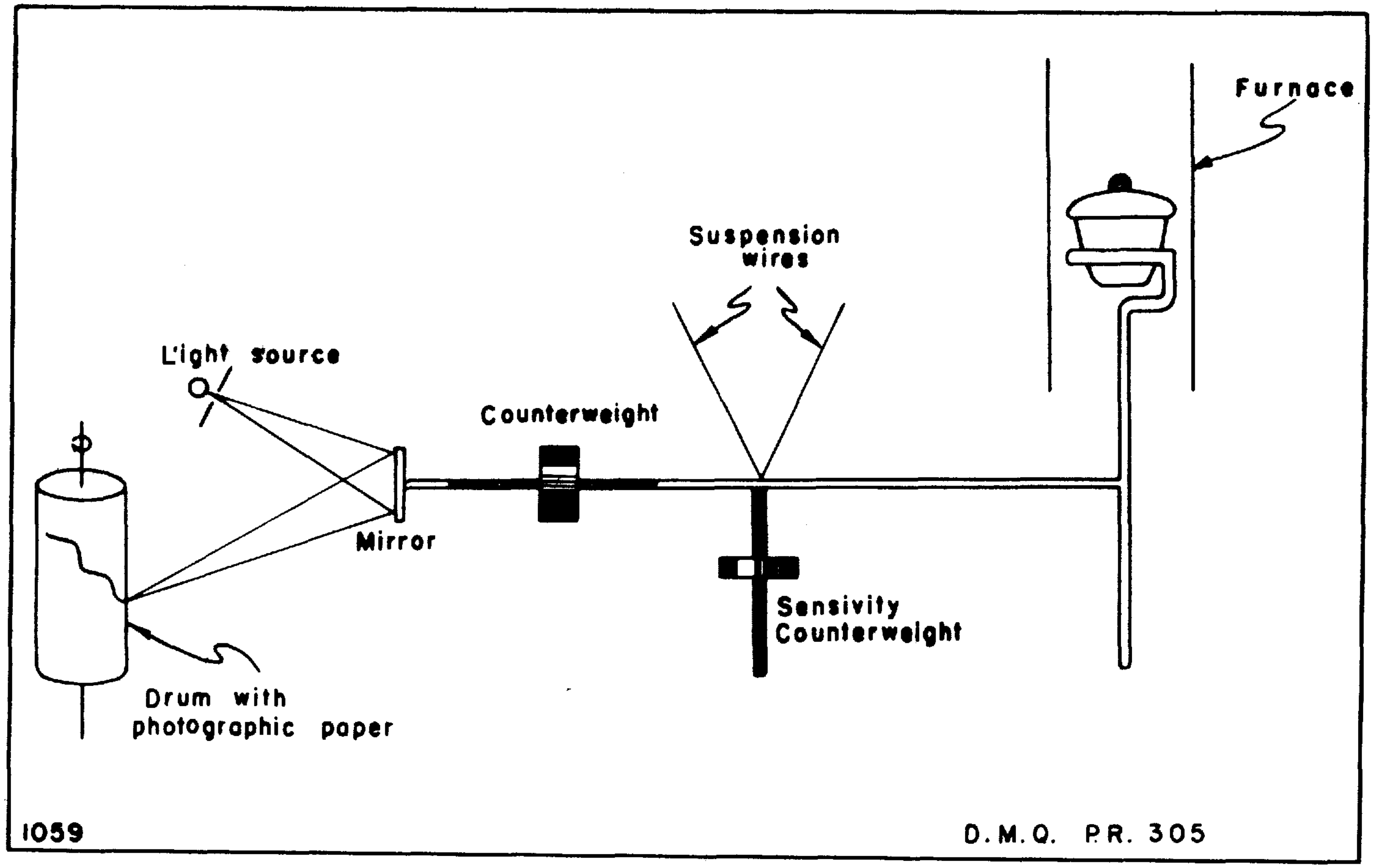

Fig. I. Schematic diagram of the Chevenard Thermobalance.

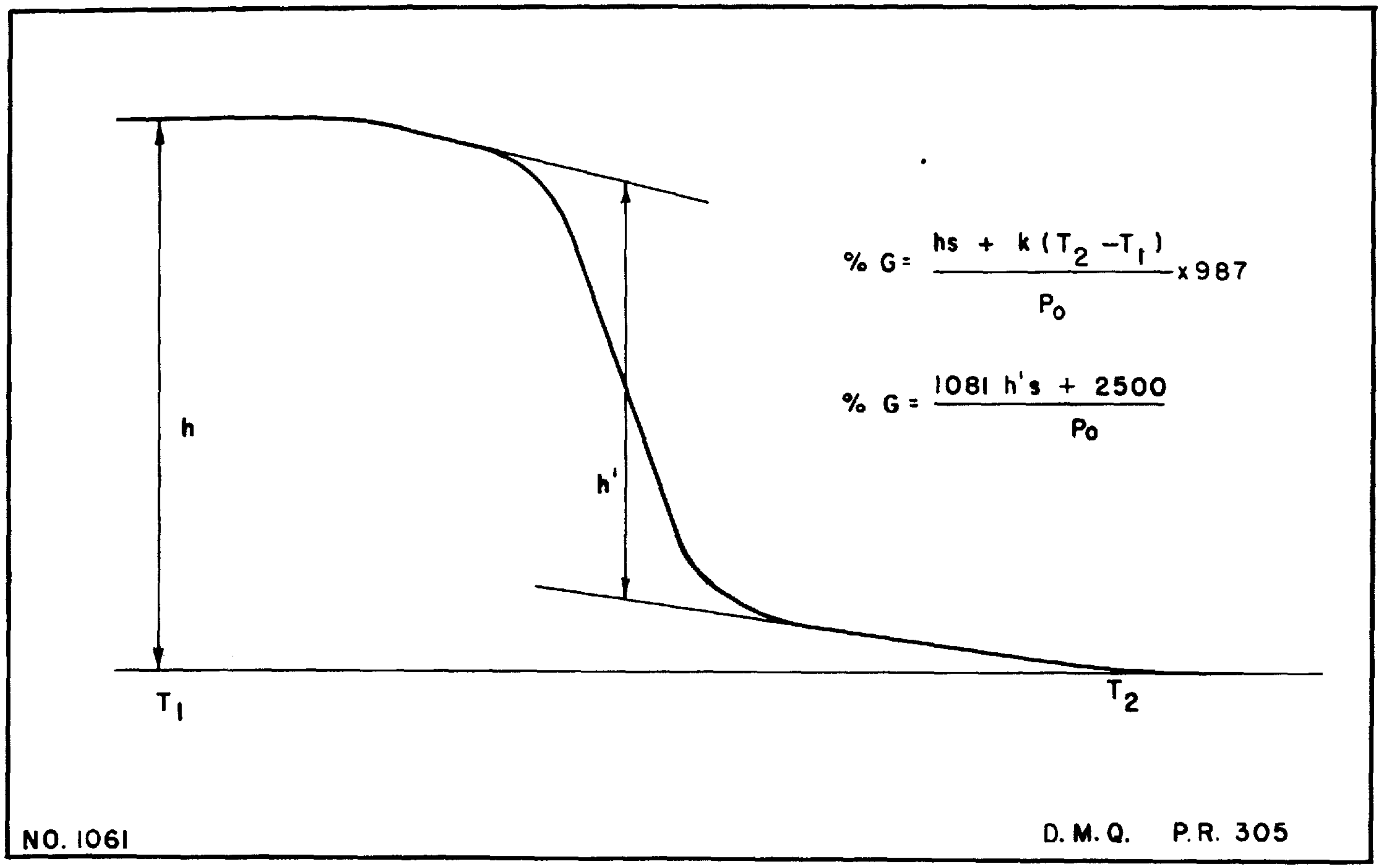

Figure 2. Thermogram of Goethite

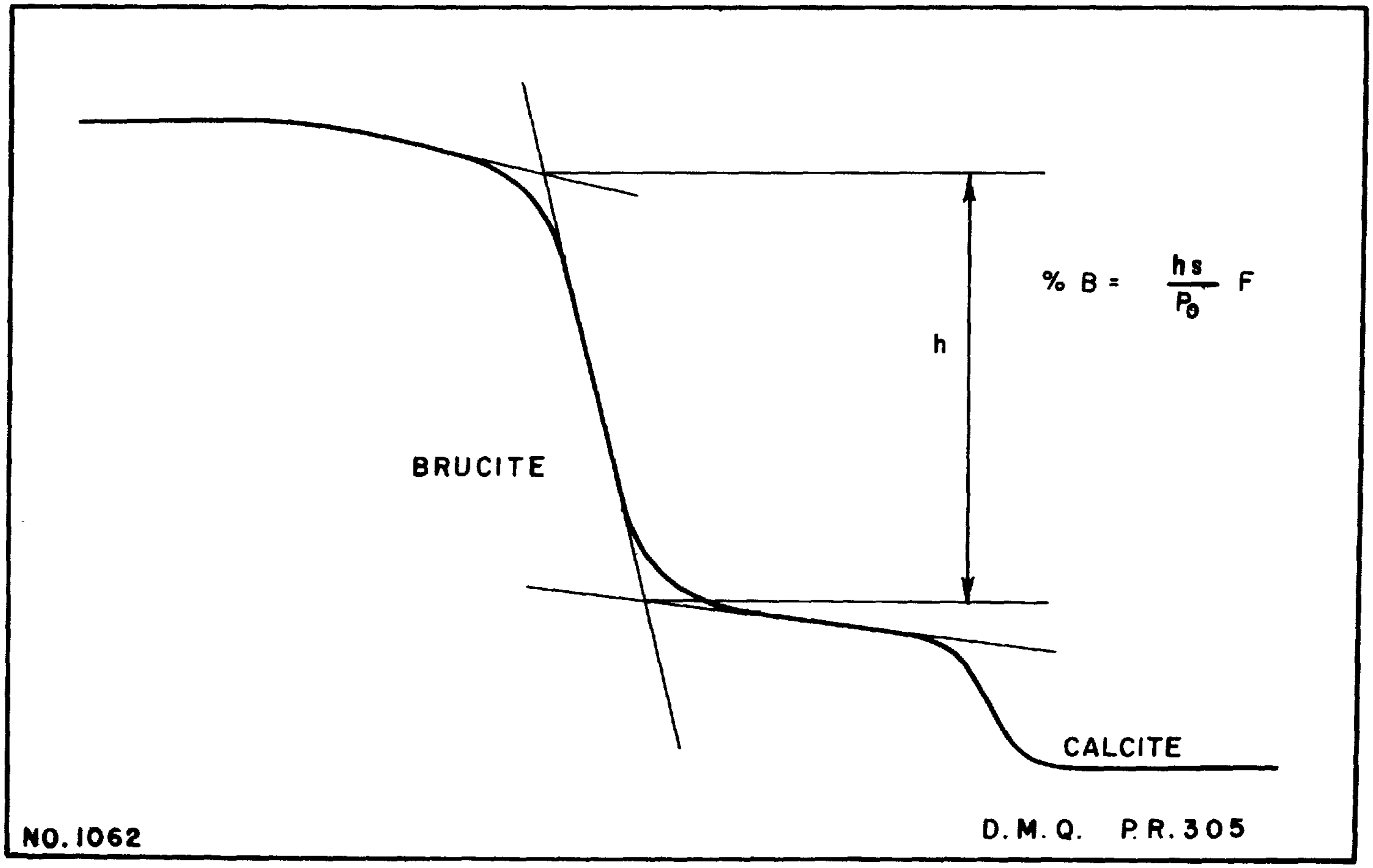

Figure 3. Thermogram of a mixture of Brucite and Calcite.

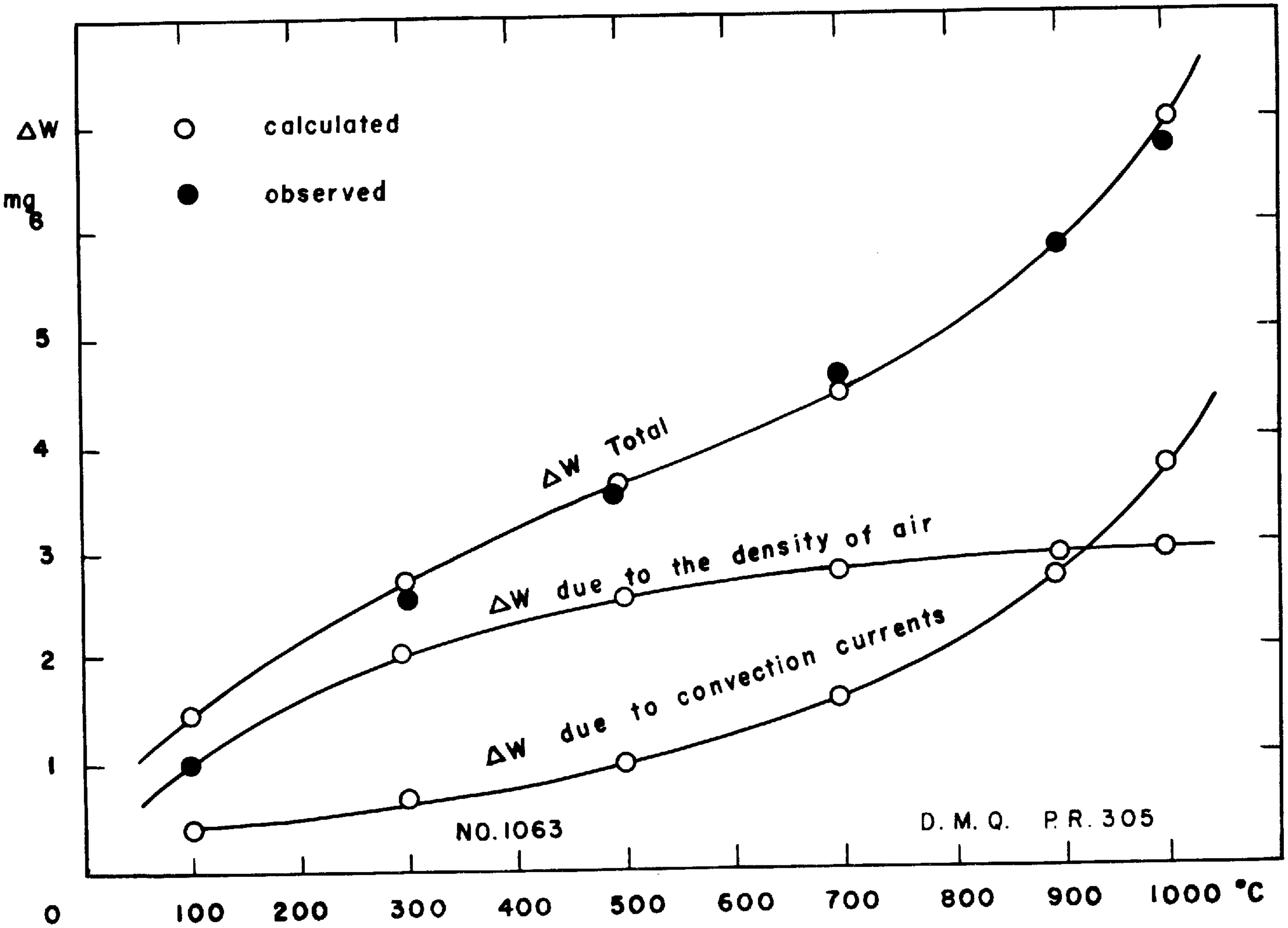

Fig. 4. Correction factor to be applied for apparent weight change due to convection currents and to the density of air.

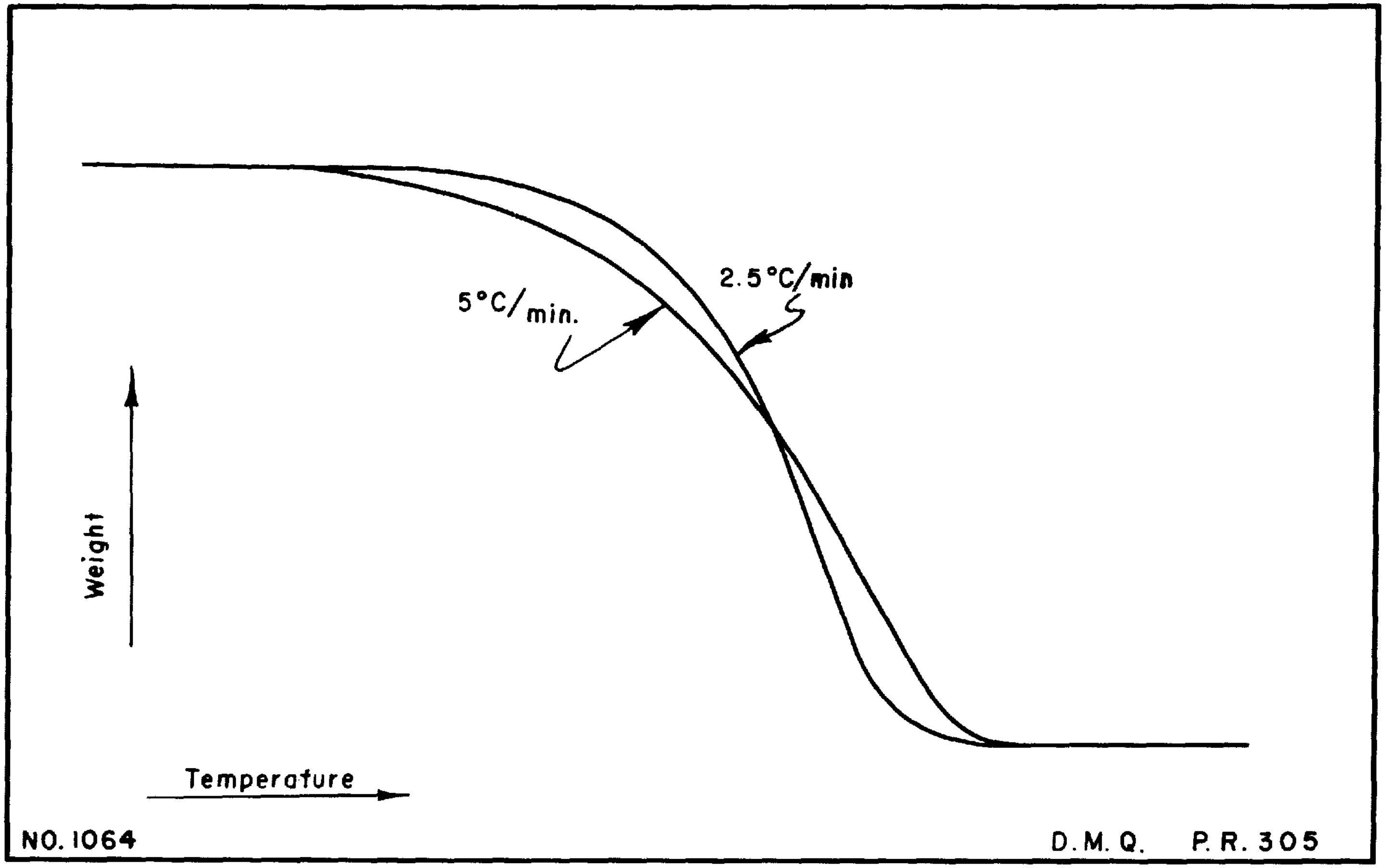

Figure 5. Effect of rate of heating on the dehydration curve of Brucite.