A THERMOGRAVIMETRIC ANALYZER FOR CORROSIVE ATMOSPHERES, AND ITS APPLICATION TO THE CHLORINATION OF ZrO_2-C MIXTURES

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ABSTRACT

We report on a thermogravimetric analyzer built on the basis of a Cahn 2000 electrobalance, suitable for using with corrosive atmospheres. We discuss the corrections for buoyancy and gas-flow effects, which strongly modify the thermogravimetric curves.

As an application, we have studied the kinetics of a reaction between chlorine and a mixture of zirconia and carbon. We have been able to measure the uptake of chlorine by carbon and the reaction rate within the first 50 seconds. We present evidence of a transition to quite a different reaction rate at longer times.

INTRODUCTION

Thermogravimetry (TG) has been extensively used for the study of kinetics of gas-solid reactions, e.g. for determining reaction mechanisms, and kinetic parameters relevant in technological applications.

Many interesting reactions in extractive metallurgy involve corrosive gases. This fact limits the use of some commercial high resolution thermogravimetric analyzers (TGA). Therefore we have developed our own TGA, suitable for corrosive atmospheres, on the basis of a Cahn 2000 electrobalance.

The measurement of weight changes in the range of micrograms is hampered by several effects [1-5] such as buoyancy [3,5], gas flow effects [7], thermomolecular flow effects (TME) [2, 4, 6], free gas convection [4, 8], electrostatic effects [7], zero drift [4, 9], etc.

An appropiate design of the hangdown tube reduces some of these disturbing effects, such as free gas convection and electrostatic effects [1, 3, 9]. Buoyancy, TME and gas flow effects can be compensated in symmetrical TGA [1, 9, 10]. However, under corrosive atmospheres it is advisable not to use a symmetrical TGA because the corrosive gas might circulate between the hangdown tubes, and damage the weighing unit of the electrobalance.

Therefore, most of high accuracy TGA for corrosive atmospheres reported in the literature are asymmetrical [11, 12, 13]. On the

other hand, the use of asymmetrical TGA requires a calibration TG curve (using an inert sample of the same volume as the actual sample) for each set of experimental conditions, e.g. gas flow, heating rate, sample size, gas composition, etc.

The purpose of the present paper is to demonstrate the perfomance of our asymetrical TGA by measuring the chlorination kinetics of ZrO_2 in presence of C, using non-isothermal and isothermal techniques. The reaction which takes place [14] at temperatures above 400 C may be represented by:

$$ZrO_2(s) + 2\ Cl_2(g) + 2\ C(s) \longrightarrow ZrCl_4(g) + 2\ CO(g) \qquad (1)$$

Different mechanisms for this reaction have been suggested [15,16], however a comprehensive model of this reaction does not exist. We present in this work preliminary results on the reaction rate which were obtained through a careful evaluation of the systematic errors involved in thermogravimetric techniques.

EXPERIMENTAL SYSTEM

Fig. 1 shows a block diagram of the TGA system constructed on the basis of a Cahn 2000 electrobalance. This electrobalance has a sensitivity of 0.1 ug and a mechanical and electrical tares of 1 g and 100 mg respectively. The sample is contained in a quartz crucible which hangs from one of the arms of the balance by means

of a quartz wire. The mechanical counterweight hangs on the other arm. A quartz hangdown tube, which is similar to one previously described by one of us [9], carries the gases to the sample. This design [9] reduces the effects of aerodynamic forces acting on the crucible, as well as increases the linear velocity of the gas mixture in the zone of the furnace, where the higher gradient of temperature exists. This reduces undesirable thermal segregation effects [18]. The outer surface of the hangdown tube is painted with Pt paint over a lenght of 10 cm and electrically grounded in order to eliminate electrostatic forces. The temperature of the sample is measured using a Pt-Pt 10%Rh thermocouple encapsulated in quartz, which is placed 2 mm below the crucible.

An electrical furnace controlled by means of a PID regulator controls the temperature of the sample, which we can vary from room temperature up to 1200 C. The maximum noise of the TGA system is 5 ug peak-to-peak at 1100 C under a flowrate of 9 l/h (NTP). The weighing unit is protected from the corrosive action of chlorine by a stream of argon (see fig. 1). At the exit of the weighing unit this Ar stream mixes with Cl_2 generating the reactive mixture which circulates in the hangdown tube downstream, as is illustrated in fig. 1. The reaction products which condense at room temperature are collected in the bottom of the hangdown tube. The gas flowrate and composition are controlled by means of a Matheson multiple flow controller.

The data acquisition is performed by means of a IBM PC/XT

computer using a Data Translation DT 2805 interface. This interface also allows programming the furnace temperature.

EXPERIMENTAL PROCEDURE

In our experiments we used the smallest possible specimens which were compatible with accurate measurements, as is usually recommended in TG experiments [19, 20]. The high sensitivity of our TGA system allowed us to perform the kinetic studies using samples of 2 to 10 mg. As we explain later, samples of 10 mg were large enough to observe the uptake of chlorine by C. The samples were prepared by a mechanical mixing of ZrO_2 powder and carbon powder. The starting materials were ZrO_2 99.9% purity (Koch-Light Labs.) with a BET surface area of 4.5 m^2/g, and carbon with a BET surface area of 17.5 m^2/g. Carbon was obtained by thermal decomposition of sucrose (Mallinckrodt Chemical Works).

In order to eliminate any spurious volatile substances the samples were previously heated at 950 C in a circulating argon atmosphere. Then the temperature and flowrate were adjusted to the values corresponding to the beginning of the experiment, and subsequently the reactive gas was introduced.

The gases used were Ar 99.99% purity (AGA Argentina) and Cl_2 99.9% purity (Indupa Argentina).

All operational control, data acquisition and manipulation was done through the computer. The data were acquired every 0.1 s.

This rate is compatible with the period of the Cahn 2000 electrobalance.

CORRECTIONS

a) Buoyancy

In order to determine the absolute mass of the sample it is necessary first to determine buoyancy effects [21].

Fig. 2 shows the correction curve due to buoyancy determined with an empty crucible in a static Ar atmosphere under a pressure of 700 torr. The mass gain is about 170 ug at 950 C. This value is three orders of magnitude higher than the sensitivity of the electrobalance and represents about 10% of the smallest sample mass used in our experiments. In view of the small size of our samples their contribution to the total buoyancy effects were neglected.

b) Flow effects

Non-isothermal kinetics is based on determining the mass change of the sample under a fixed heating rate in a given atmosphere. Typical corrections are shown in fig. 3., where we plot the apparent mass change as a function of temperature under a chlorine partial pressure (PCl_2) of 244 torr and a heating rate of 10 C/min, for three differents flowrates, (a,b,c).

It is evident that the apparent mass-gain due to flow effects is higher than that due to buoyancy, fig.2.

c) Apparent mass change due to a simultaneous change in composition and flowrate of the gaseous atmosphere at constant temperature.

In heterogenous kinetics it is often useful to determine the initial reaction rate, which may give valuable information about the reaction mechanism. In this case the kinetic study is performed under isothermal conditions. The sample is kept at constant temperature in an inert gas atmosphere and then the reactive gas is introduced into the reactor. This produces a change in gas composition and gas flowrate which disturbs the measurements. In fig. 4 we show the apparent mass change of an empty crucible at 950 C, when a flowing Ar atmosphere of 1.32 l/h is disturbed by the injection of two different flowrates of chlorine. This apparent mass change must be taken into account when correcting the kinetic data obtained during the early stages of the reaction.

RESULTS AND DISCUSSION

A) Non-isothermal kinetics

Curve "a" in fig. 5 shows the TG curve obtained using 2 mg of sample containing 20% w/w of carbon. This curve corresponds to a heating rate of 10 C/min, and a flowrate of 8.37 l/h under PCl_2 = 250 torr. The heating was made starting from 400 C, since

$ZrCl_4$ is solid at lower temperatures.

Curve "b" shows the thermogram obtained after the correction by apparent mass-gain.

It is seen that the original curve is strongly modified by the apparent mass-gain. No change in mass is detected below 700 C, but at higher temperatures the reaction rate is appreciable.

B) Isothermal kinetics

Here we shall only report on the kinetic behaviour observed during the first 150 seconds.

Curve "a" in fig. 6 shows the mass evolution of a sample of 10 mg (containing 70% w/w of carbon), at 950 C, under a PCl_2 = 300 torr, as directly given by the TGA. Curve "b" shows the results after correcting for apparent mass-change. This correction is done by software following the calibration curves previously discussed. The zero on the time scale corresponds to injection of Cl_2 in the reactor. During the first 25 seconds no change in mass is observed, corresponding to the time necessary for chlorine to reach the sample. Then a small increase in mass of about 40 ug occurs, followed by a rapid mass loss of about 1 mg, and then the reaction slows down appreciably.

i) Chlorine uptake by carbon.

In view of the fact that we have corrected for apparent mass-change, the increase in mass shown in fig. 6,"b" is real and will be related to reaction between the gas phase and the sample.

Since the adsorption of Cl_2 on ZrO_2 has been shown [22] to be negligible under the present experimental conditions, we only need to consider the interaction between Cl_2 and carbon. The chlorine uptake on carbon was determined by studying a sample of pure carbon under the same experimental conditions. The measured mass gain for 7 mg of sample is reported in fig. 7, curve "a". The initial uptake is very fast. The final mass gain is significant and reachs a value of about 7% of the total carbon mass. Clearly this uptake is larger than the suggested by the mass gain observed in fig. 6, "b".

ii) Rate of $ZrCl_4$ formation.

We have analysed curve "b" in fig. 6 in terms of the superposition of two independent and simultaneous phenomena : a mass gain due to the uptake of chlorine by carbon, and a mass loss due to the formation of gaseous $ZrCl_4$. In order to consider only the mass change due to $ZrCl_4$ formation, we subtract from curve "b", fig 6 the mass gain due to the uptake of chlorine by carbon. The result is represented by curve "c" of fig. 7, which gives the mass loss due to formation of $ZrCl_4$ only. In the same plot we also present, for comparison, curve "b" from fig. 6.

The slope of curve "c" gives the reaction rate of $ZrCl_4$ formation only. There is a transition from a high reaction rate to a low rate. Point "P", obtained by a linear extrapolation of the high-rate and low-rate parts of the curve may be used to measure the extent of the reaction when the transition ocurrs. A mass balance based on equation 1 shows that at point "P" 42 % of

the ZrO_2 has reacted. Aditional results [23] suggest that the fraction of unreacted ZrO_2 depends strongly upon reaction temperature and PCl_2.

CONCLUSIONS

We have shown the perfomance of a high resolution TGA, suitable for using with corrosive atmospheres. The equipment allowed us to get accurate information on the initial reaction rate and chlorine uptake phenomena by carbon when studying the chlorination of a zirconia-carbon mixture. A discussion of the corrections for various types of errors has also been given. Additional results, and a discussion of the kinetics of chlorination of ZrO_2-C mixtures will be presented in a forthcoming paper [23].

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Figure 1 : Schematic of thermogravimetric analyzer. M, manometer; V, needle valve; D, drying column; U-M, U-tube manometer; G, on-off valve; T, three-way valve; 1: Bottle with SO_4H_2, used as an automatic pressure relief valve; 2: Exit of gases to hood; 3: drying tube; 4: flowmeters; 5: electrobalance; 6: jacket for condensation of eventual vapors; 7: radiation shields ; 8: hangdown tube; 9: furnace; 10: closed-end quartz sheath for thermocuple; 11: collector for eventual liquids products.

Figure 2 : Apparent mass-gain due to buoyancy for an empty crucible in a static Ar atmosphere as a function of temperature.

Figure 3 : Apparent mass-gain for an empty crucible in a flowing mixture Ar-Cl_2 (PCl_2 = 244 torr) as a function of total flowrate, using a heating rate of 10 C/min.

Figure 4 : Apparent mass for empty crucible at injection of chlorine to the reactor, as a function of chlorine flowrate, at 950 C.

Figure 5 : Non-isothermal curves: a) empty crucible. b) 2 mg of mixture ZrO_2-C (20% w/w of carbon).

Figure 6 : Isothermal mass loss of 10 mg of mixture ZrO_2 (70% w/w of carbon) at 950 C and PCl_2 = 300 torr. Data obtained during the first 150 seconds.

Figure 7 : Mass change due to the interaction of Cl_2 a) pure carbon. b) reaction with mixture ZrO_2-C (same plot as fig 6, "b"). Curve "c" shows the result of subtracting "b" from "a".

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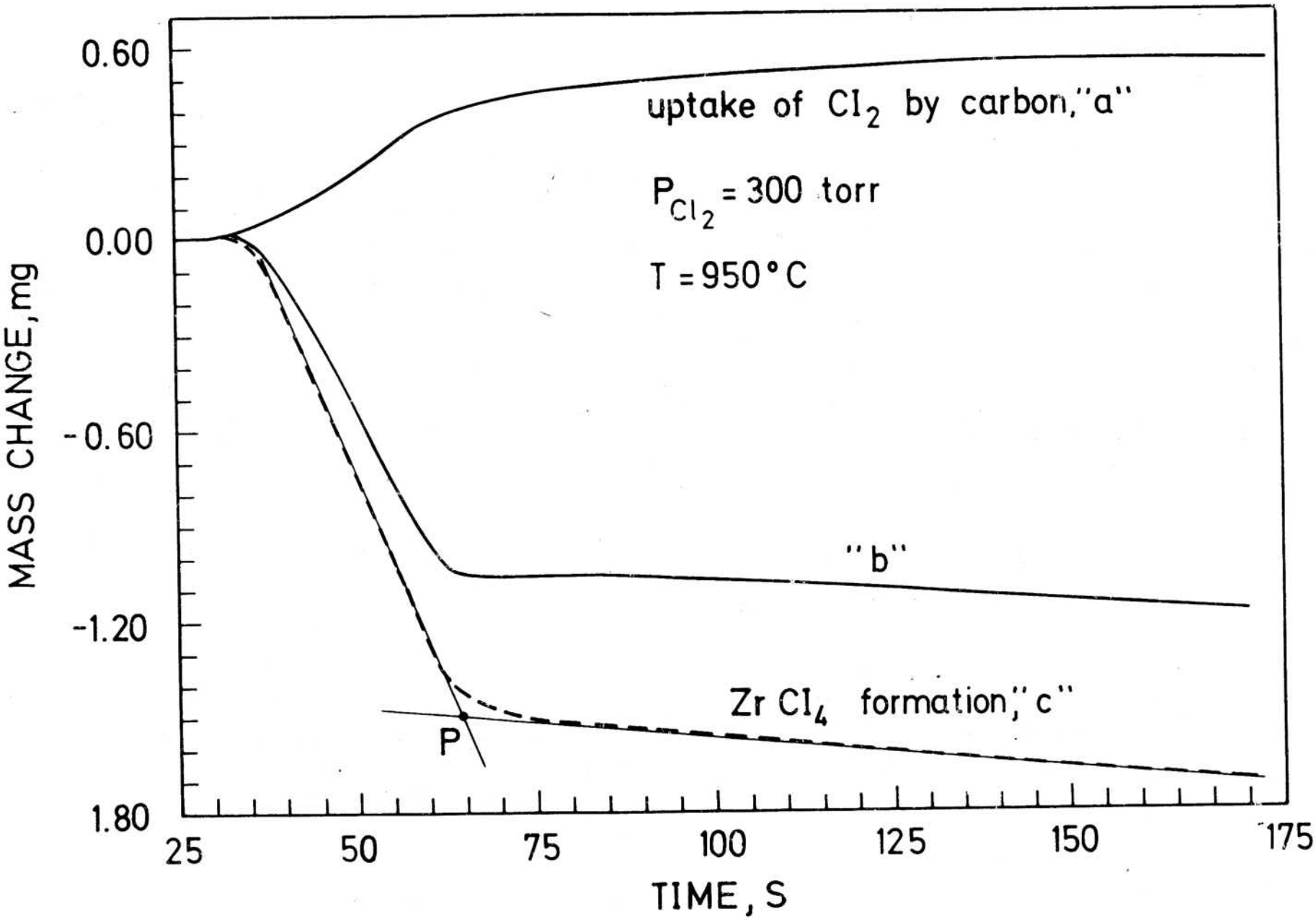
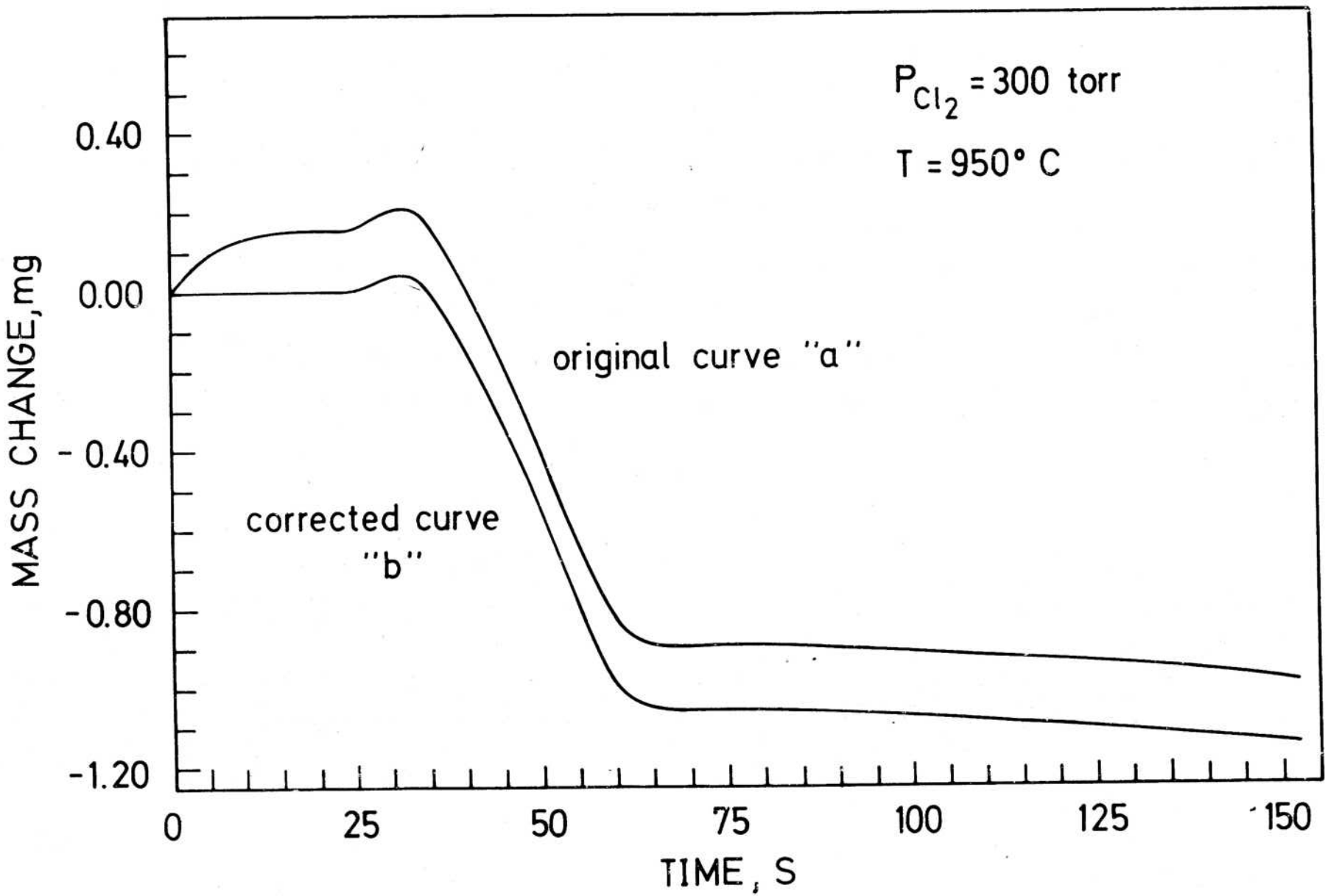

0.60
0.00
-0.60
-1.20
1.80
MASS CHANGE, mg
uptake of Cl_2 by carbon, "a"
P_{Cl_2} = 300 torr
T = 950 °C
"b"
Zr Cl_4 formation; "c"
P
25
50
75
100
125
150
175
TIME, S


P_{Cl_2} = 300 torr
T = 950° C
original curve "a"
corrected curve "b"
MASS CHANGE, mg
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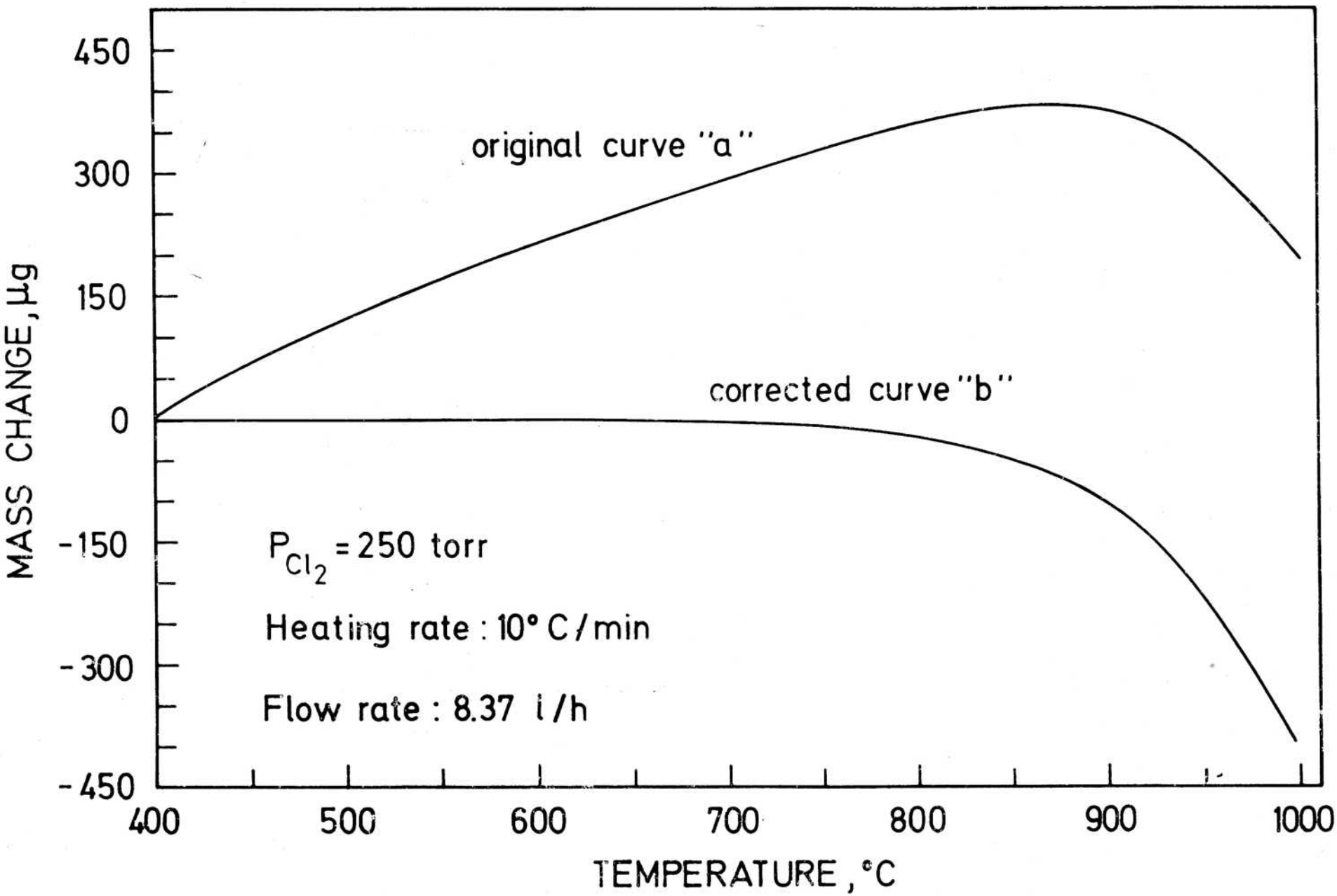
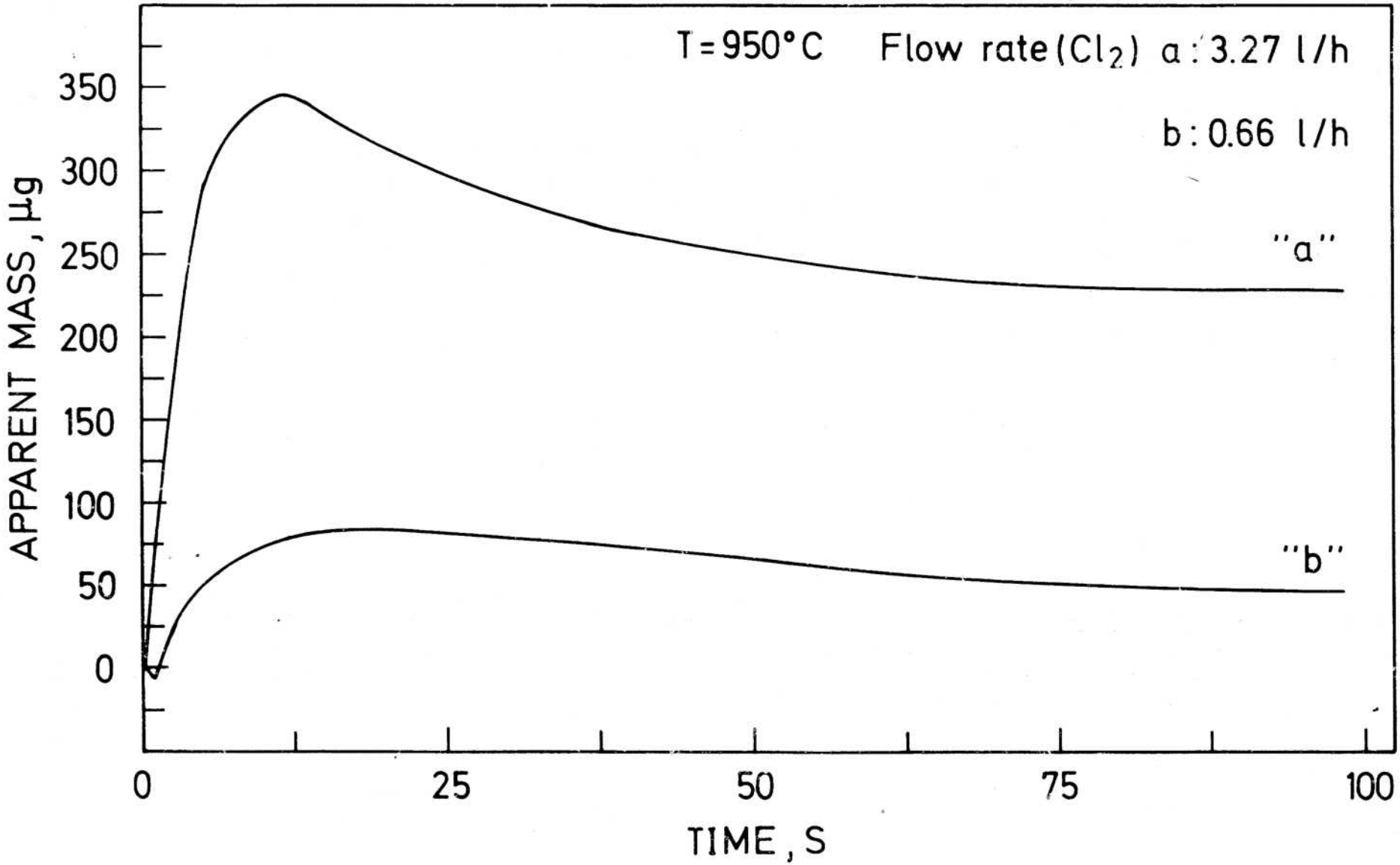
- 0.40
-0.80
-1.20
0
25
50
75
100
125
150
TIME, S


450
300
150
0
-150
-300
-450
MASS CHANGE, µg
original curve "a"
corrected curve "b"
P_{Cl_2} = 250 torr
Heating rate : 10° C / min
Flow rate : 8.37 l / h
400
500
600
700
800
900
1000
TEMPERATURE , °C


T=950°C Flow rate(Cl2) a: 3.27 l/h
b: 0.66 l/h
"a"
"b"
APPARENT MASS, µg
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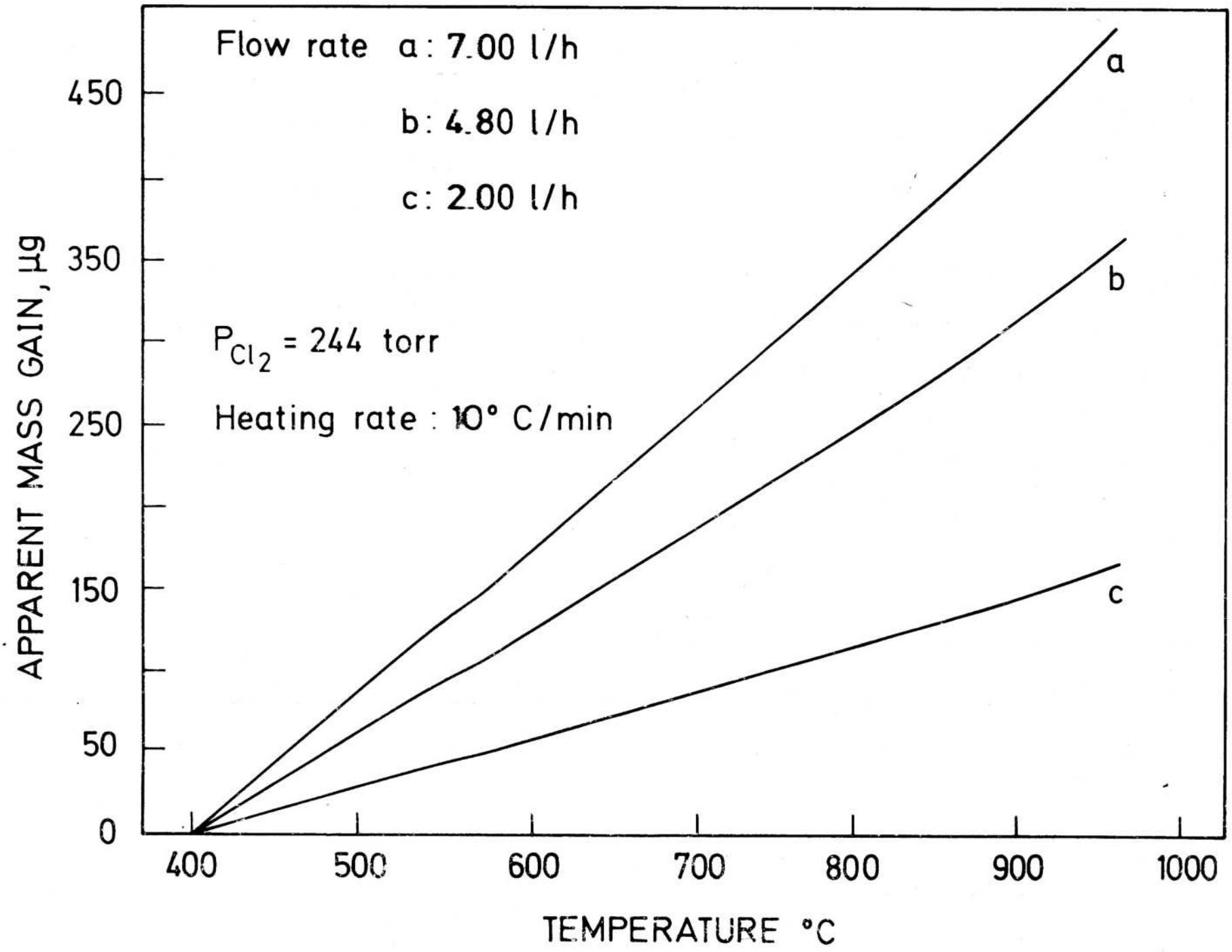
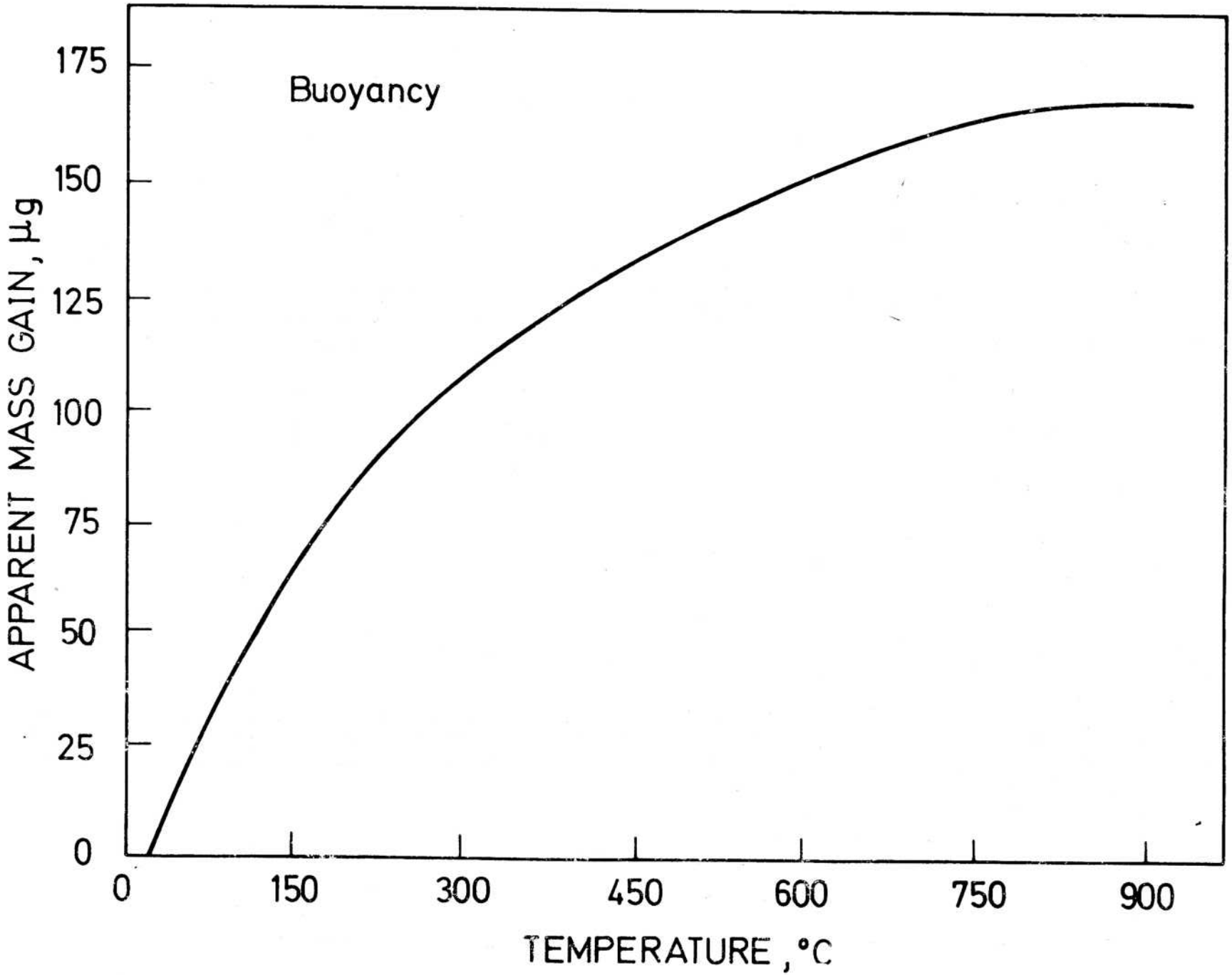
300
250
200
150
100
50
0
0
25
50
75
100
TIME, S


Flow rate a: 7.00 l/h
b: 4.80 l/h
c: 2.00 l/h
P_{Cl_2} = 244 torr
Heating rate : 10° C/min
a
b
c
APPARENT MASS GAIN, µg
0
50
150
250
350
450
400
500
600
700
800
900
1000
TEMPERATURE °C


Buoyancy
APPARENT MASS GAIN, µg
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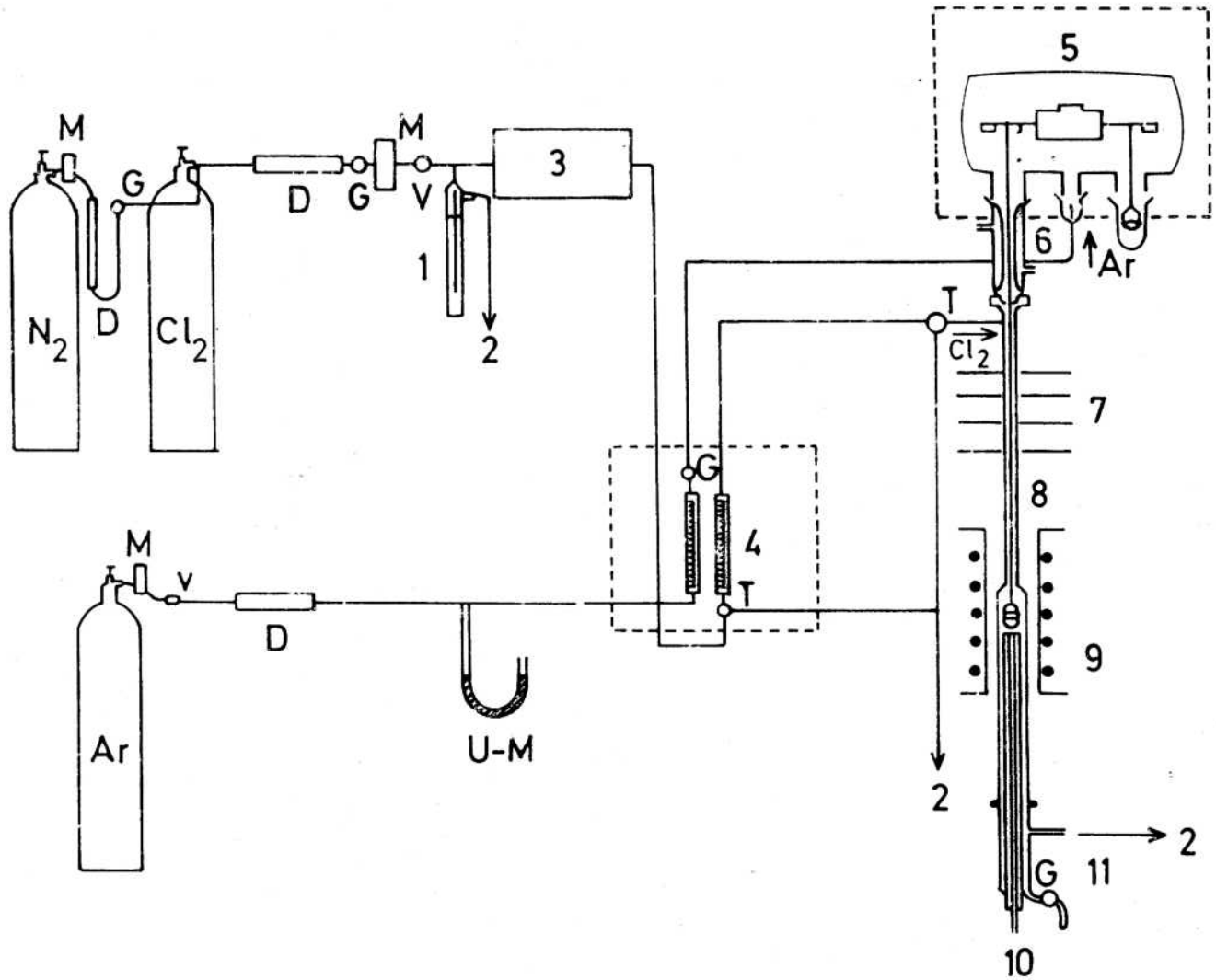
150
125
100
75
50
25
0
0
150
300
450
600
750
900
TEMPERATURE, °C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4
T
M
v
D
9
Ar
U-M
2
2
G
11
10