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**EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM**

**SOME CONSIDERATIONS ON THE GRAVIMETRIC  
DETERMINATION OF THE OXYGEN TO METAL RATIO  
IN PLUTONIUM OXIDES AND MIXED  
URANIUM-PLUTONIUM OXIDES**

by

**M. J. MAURICE and K. BUIJS**

**1969**



**Joint Nuclear Research Center  
Karlsruhe Establishment - Germany**

**European Transuranium Institute**

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## ABSTRACT

The determination of the oxygen to metal ratio in plutonium oxides and mixed uranium - plutonium oxides is described. The sample is weighed, equilibrated with air or a mixture of carbon monoxide and carbon dioxide respectively at 850 - 900°C, and reweighed. Results obtained with more than 130 samples are analysed and special attention is paid to the influence of the precision of the weighing on the precision of the final result. The influence of different possible types of inhomogeneity in samples is discussed.

## KEYWORDS

GRAVIMETRY  
DETERMINATION  
OXYGEN  
WEIGHT  
PLUTONIUM OXIDES  
URANIUM OXIDES  
MIXTURES  
EQUILIBRIUM  
AIR  
CARBON MONOXIDE  
CARBON DIOXIDE

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## 1. Introduction (\*)

In our institute we needed a simple and precise method for the determination of the oxygen to metal ratio in large series of plutonium oxide and mixed uranium plutonium oxide samples. In accordance with the conclusion reached by LYON (6.1) in his review of available methods, we decided to adopt a gravimetric method for this purpose. The principle of this method is that the sample is equilibrated with such an atmosphere as to yield an oxide of well-defined composition, e.g. an oxygen to metal ratio of 2.000. In the case of pure plutonium oxide and pure uranium oxide oxidation in air to  $\text{PuO}_2$  and  $\text{U}_3\text{O}_8$  respectively can be applied. For analysis of mixed oxides, however, the oxidized state  $\text{PuO}_2 - \text{U}_3\text{O}_8$  cannot be used as a reference state since the oxygen take-up is less than expected (6.2).

MARKIN and coworkers (6.3, 6.4) determined the relation between the oxygen potential,  $\Delta\bar{G}(\text{O}_2) = -RT \ln P_{\text{O}_2}$  and the oxygen to metal ratio at different temperatures for a series of uranium - plutonium ratios in mixed oxides. In this investigation only samples containing at most 30 % of plutonium oxide were involved. Fig. 1 shows some typical results. At the stoichiometric composition, the oxygen to metal ratio is seen to be rather insensitive to small variations in the oxygen potential and in the temperature. From graphs showing the oxygen potentials of appropriate gas mixtures such as hydrogen-water and carbon monoxide - carbon dioxide, as functions of temperature, the proper conditions for obtaining stoichiometric compositions can be chosen.

In the case of uranium oxide, the method gave the same results as a polarographic method, applied after dissolution of the sample (6.4). For mixed oxides the accuracy was assured by MARKIN's definition of stoichiometric mixed uranium - plutonium oxides, i.e. the oxide resulting from equilibration with a carbon monoxide - carbon dioxide mixture at  $850^\circ\text{C}$  (6.3).

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(\*) Manuscript received on 3 June 1969.

However, care should be taken in the analysis of samples containing more than 30 % of plutonium oxide since accurate calibration data are not available for these compositions.

It should be noted that normal polarographic and coulometric procedures cannot be applied to the analysis of plutonium oxides and mixed oxides, since it is impossible to dissolve these samples without any oxidation occurring.

In our laboratory we apply the gravimetric method on a routine basis. For economical reasons it was decided to apply an oxidation in air to pure plutonium oxides and to analyse uranium oxides and mixed oxides by equilibration with a mixture of carbon monoxide - carbon dioxide. Three types of balances were used, viz. a Mettler balance type H15, a Sartorius balance, type 1701 and a Mettler balance M5 SA. The corresponding procedures will be called macro-, semimicro- and micromethod.

In this report our experience with the method is described and discussed. Special attention will be paid to the influence of the precision of the weighing on the precision of the final result. As the microbalance was finally chosen for routine measurements, a more detailed study has been made of the precision attainable using this balance.

## 2. Description of apparatus

A scheme of the apparatus is given in fig. 2. With this apparatus it is possible to heat the sample in the carbon monoxide - carbon dioxide mixture, in argon and in air. The choice between the three possibilities is made by turning the stopcocks A and B.

Argon is purified by passing it over copper (II) oxide at  $350^{\circ}\text{C}$  in furnace  $F_1$  in order to eliminate traces of reducing substances and then over sodium hydroxide pellets

(column N) and a mixture of silicagel and molecular sieves (column S) for the absorption of traces of carbon dioxide and water. Traces of oxygen are eliminated by passing the argon over copper at 600°C in furnace F<sub>2</sub>. Argon is used to provide the atmosphere in which the sample cools down to room temperature. The purification described proved to be indispensable: without it inconsistent results were obtained.

The carbon monoxide - carbon dioxide mixture is also passed over copper at 600°C in furnace F<sub>2</sub> in order to decompose iron carbonyls contained in it. The free energy change  $\Delta G = -RT \ln P_{O_2}$  for the reaction  $2 \text{Cu} + 1/2 \text{O}_2 \rightleftharpoons \text{Cu}_2\text{O}$  at 600°C amounts to 50 kcal per mole (6.5), which means that copper is not oxidized by the carbon monoxide - carbon dioxide (10 + 1) mixture ( $\Delta G = -108$  kcal per mole) at this temperature and that the composition of the gas mixture is not affected by this operation.

After having used the apparatus for some time without furnace F<sub>2</sub> a deposit of iron in the tube of furnace F<sub>3</sub> was observed. This phenomenon was explained by the formation of iron carbonyls, probably from iron of the CO/CO<sub>2</sub>-cylinder, and subsequent decomposition at the high temperature prevailing in furnace F<sub>3</sub>. In order to prevent deposition of iron on the sample the CO/CO<sub>2</sub>-mixture was passed through furnace F<sub>2</sub>, where in fact a deposit of iron was observed. Between the furnaces F<sub>2</sub> and F<sub>3</sub>, the gas mixture does not touch iron, except for a filter out of porous stainless steel at the place where the gas enters into the glove box. The materials used for the gas supply system are copper, perspex, polyvinylchloride, glass and silica.

Samples are equilibrated in furnace F<sub>3</sub> which is placed in a glove box under a nitrogen atmosphere containing at most 50 ppm of water vapour and 0.5 % of oxygen.

When the microbalance was tested under normal laboratory conditions outside the glove box, the standard deviation of a single weighing (including adjustment of zero) was found to be  $2.7 \mu\text{g}$  (the number of degrees of freedom,  $\nu$ , is 55). In the especially fortified glove box with slight underpressure and the usual ventilation, a standard deviation of  $3.1 \mu\text{g}$  was found ( $\nu = 37$ ). These figures do not include the contributions of day-to-day variations.

### 3. Selection of conditions

The conditions for equilibrating the sample were fixed on the basis of MARKIN's work (6.3). The gas mixture used consisted of 10 parts of carbon monoxide and 1 part of carbon dioxide. Temperature was fixed at  $850 - 900^\circ\text{C}$ . To ensure a complete reaction the samples were equilibrated overnight.

Samples were not dried prior to equilibration. From a recent investigation (6.6) it followed that a temperature of at least  $300^\circ\text{C}$  is required for quantitative desorption of water from the mixed oxides. In order to avoid a change in composition of a sample before the measurement, it was decided not to dry the sample and to correct the result for the water content, determined separately.

The conditions for weighing samples on the microbalance were fixed on the basis of the following data.

The standard deviation of a single weighing, including the day-to-day variations, amounts to  $11.0 \mu\text{g}$  ( $\nu = 30$ ). Unfortunately, it was not possible to correlate the daily variations to any such parameters as temperature or pressure. The difference in weight between two pieces of platinum, however, measured during a 50-day period gave a standard deviation of  $3.7 \mu\text{g}$  ( $\nu = 15$ ). From these figures it follows that the precision of a weighing as applied to the determination of the oxygen to metal ratio can be

substantially improved if all sample weights are compared to a reference weight.

The reaction  $2 \text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$  can give rise to deposition of carbon from a  $\text{CO}/\text{CO}_2$ -mixture (10 + 1) as soon as temperature drops below  $800^\circ\text{C}$  (6.7). If the sum of the  $\text{CO}$  and  $\text{CO}_2$  partial pressures is lower than 1 atm the deposition sets in at a lower temperature. From this data it follows that replacement of the  $\text{CO}/\text{CO}_2$ -mixture (10 + 1) by argon at  $850^\circ - 900^\circ\text{C}$  and subsequent cooling eliminates the risk of carbon deposition onto the oxide sample. If we assume that the oxygen partial pressure in the argon is of the order of  $10^{-13}$  atm as determined by the temperature of the copper in furnace  $F_2$ , it follows that from the quantity of argon used in cooling, viz 90 Nl, only about  $10^{-12}$  g of oxygen can be taken up by the sample, which at  $900^\circ\text{C}$  is in equilibrium with an oxygen partial pressure of about  $10^{-19}$  atm.

#### 4. Procedures

##### 4.1 Macro and semimicro procedure

Carry out all manipulations in an inert atmosphere containing no more than 50 ppm of water vapour. In a platinum boat weigh out 100 to 500 mg of sample and transfer the boat with sample to the center of the heating tube in furnace  $F_3$  (see fig. 2). Pass a stream of air - in the case of plutonium oxides - or carbon monoxide - carbon dioxide mixture (10 + 1) - in the case of uranium oxides and mixed uranium - plutonium oxides - through the tube at a rate of 30 Nl per h. Heat to  $850 - 900^\circ\text{C}$  and keep at this temperature overnight. Replace the  $\text{CO}/\text{CO}_2$ -stream by an argon stream, cool to room temperature and weigh.

Calculate the oxygen to metal ratio,  $[\text{O}/\text{M}]$ , according to

$$\left[ \frac{\text{O}}{\text{M}} \right] = 2 - \frac{\text{M}}{16} \left\{ \frac{p-q - w(p-t) 10^{-6}}{t - q} \right\} \quad (\text{I})$$

where M = molecular weight of the sample after equilibration

p = weight of the platinum boat with sample before equilibration

q = weight of the platinum boat with sample after equilibration

t = weight of the empty platinum boat

w = water content in ppm

#### 4.2 Microprocedure

Follow essentially the procedure described above but carry out the weighings as follows.

Between the weighing aimed at determining the values of p and t, weigh a piece of platinum which serves as a reference weight. Choose the size of this piece of platinum such that its weight is comparable to that of the sample boat. Weigh the same piece of platinum again shortly before or after weighing back the sample. Calculate the oxygen to metal ratio  $\left[ \frac{O}{M} \right]$ , according to

$$\left[ \frac{O}{M} \right] = 2 - \frac{M}{16} \left\{ \frac{(p-r_1) - (q-r_2) - w(p-t) 10^{-6}}{(t-r_1) - (q-r_2)} \right\} \quad (II)$$

where  $r_1$  = reference weight before equilibration of the sample

$r_2$  = reference weight after equilibration of the sample

#### 5. Results and discussion

The procedures mentioned in sect. 4 were applied to 137 plutonium oxide and uranium - plutonium oxide samples. The mixed oxide samples were prepared from mechanical blends of the oxides as well as by the coprecipitation procedure. Oxygen to metal ratios varied from 1.55 to 2.0 and from 1.87 to 2.10 respectively. Only seven uranium oxide samples were analysed in this way, since for the analysis of these samples the generally more precise

coulometric method after dissolution in phosphoric acid is in routine use in our laboratory. All samples were analysed in duplicate. Part of them were taken for production control; others had undergone special thermal treatments.

The results of three samples were not under control which was probably due to inhomogeneities. From the remaining values the standard deviations of single determinations were calculated for each of the three procedures for plutonium oxide as well as for uranium - plutonium oxides. Since an influence of the chemical composition of the sample on the precision of a procedure could not be detected on the 0.05 level, standard deviations found for the two types of samples were combined, so that finally standard deviations for each of the three procedures were obtained. The results are given in table I.

Table I

procedure	standard deviation	degrees of freedom
macro	$s_1 = 0.0056$	29
semimicro	$s_2 = 0.0029$	48
micro	$s_3 = 0.0022$	51

Between  $s_1$  and  $s_2$  and between  $s_2$  and  $s_3$  significant differences must be assumed to exist on the 0.05 - level, which means that there is an influence of the precision of the weighing on the precision of the ultimate result of the determination. The most precise results are obtained by using the microprocedure.

In order to investigate the precision of the microprocedure in more detail, an equation was derived for the standard deviation of a single determination,  $s_r$  due to the dispersion of the weighings. The following equation was found:

$$s_r = \frac{1.41 M s_t}{16 (t-q)} \quad (\text{III})$$

where  $s_t$  = standard deviation of an single weighing

Substitution of  $M = 270$  and  $s_t = 3.7/\mu\text{g}$  in eq. III yields  $s_r$  - values of 0.0009 and less for samples sizes of 100 mg and higher. This value is smaller than the  $s_3$  - value mentioned in table 1, which means that there is (are) (an) other effect(s) which contribute(s) to the final precision. A possible explanation may be found in a contribution of the nature of the sample itself, viz. when the sample is more or less inhomogeneous. In order to verify this hypothesis 16 determinations were carried out on high-fired plutonium oxide which was sieved and from which the fraction with particle size between 0.5 and 1 mm was collected. A standard deviation of 0.0010 was found, which is significantly smaller on the 0.05 - level than the  $s_3$  - value given in table 1. This means that indeed part of the dispersion is caused by a nonhomogeneity of the samples. This standard deviation implies that for sufficiently homogeneous samples results may be reported to the nearest 0.0005.

From the theory of the control charts (6.8) it follows that the upper control limit of the range,  $G$ , determined from duplicate determinations, amounts to

$$G = 3.267 \cdot 0.0010 = 0.0033 \quad (\text{IV})$$

Ranges exceeding this  $G$ -value are not under control and the corresponding samples may, therefore, be qualified not sufficiently homogeneous. When this criterion is applied to the results from which  $s_3$  was calculated and the standard deviation is recalculated from the results obtained with a homogeneous sample a value of 0.0011 is found.



From the results of the determinations on the homogeneous sample mentioned above where sample sizes varied between 100 and 500 mg an influence of the sample size on the precision as expected on the basis of eq. III, could not be detected. In order to verify this result some more determinations were carried out on the homogeneous sample taking smaller sample sizes. The standard deviations found,  $s_a$ , as well as the number of observations from which they were calculated,  $n$ , and the standard deviations calculated according to eq. III,  $s_r$ , are given in table II. In fig. 3  $s_r$  and  $s_a$  are given as a function of the sample size.

Table II

sample size	$s_r$	$s_a$	$n$
20 mg	0.0044	0.0084	7
50	0.0018	0.0047	7
100	0.0009	0.0018	5
200	0.00045	0.0006	4
300	0.00030	0.0009	3
500	0.00018	0.0008	4

From table II it follows that for sample sizes up to 100 mg the standard deviation decreases with increasing sample size. For sample sizes larger than 100 mg the standard deviation seems to be constant. So, in order to attain maximum precision, sample size should be chosen between 200 and 500 mg.

The  $s_a$ -values listed in table II are larger than the corresponding  $s_r$ -values which means that there are still other unknown sources of variation which contribute to the final precision.

The question may arise as to the nature of the inhomogeneities mentioned above. In principle two types of in-

homogeneities can be distinguished, viz. a non uniform distribution of the major constituents in the sample and a non-uniform distribution of impurities.

Let us first consider the first possibility, i.e. the variations within samples of the plutonium oxide fraction. A mixture of substoichiometric plutonium oxide and uranium oxide can be regarded as a real mixture  $(\text{PuO}_{2-x})_z (\text{UO}_2)_{1-z}$  or as a mixed crystal  $\text{Pu}_z \text{U}_{1-z} \text{O}_{2-xz}$ . Due to the fact that  $x$  is independent from  $z$ , both representations are equivalent and the  $[\text{O}/\text{M}]$ -ratio thus equals  $(2-xz)$ . The relationship between  $[\text{O}/\text{M}]$  and  $z$  is given by a straight line for each value of  $x$  (see fig. 4). From fig. 4 it is seen that the greatest changes in the oxygen to metal ratio with changes in  $z$  occur at high  $x$ -values. Mutatis mutandis the same considerations are valid for overstoichiometric samples. Thus, it may be concluded that changes in  $z$  cause the greatest changes in the oxygen to metal ratio in the case of samples which are either strongly substoichiometric or strongly overstoichiometric.

$$\text{From } \left[ \frac{\text{O}}{\text{M}} \right] = 2 \pm x z \quad (\text{V})$$

it follows that

$$\Delta z = \frac{\Delta \left[ \frac{\text{O}}{\text{M}} \right]}{x} \quad (\text{VI})$$

or

$$\Delta z_{\text{rel}} = \frac{\Delta z}{z} = \frac{\Delta \left[ \frac{\text{O}}{\text{M}} \right]}{\left| \left[ \frac{\text{O}}{\text{M}} \right] - 2 \right|} \quad (\text{VII})$$

If we consider  $\Delta [\text{O}/\text{M}] = 0.003$  as the maximum permissible difference between duplicates (see eq. IV) it follows that with an  $[\text{O}/\text{M}]$  value of  $2 \pm 0.1$ , for  $\Delta z_{\text{rel}}$  a value of 0.03 is found. However, from numerous analyses of mixed oxides samples of the type discussed here, it must be concluded that such variations are very unlikely to occur under normal processing conditions.

Indeed we find for sintered mixed oxide samples, prepared from mechanical blends a standard deviation of a single determination of 0.0027, calculated from duplicate determinations on 18 samples. This value is less than the maximum permissible difference between duplicates. This means that by normal mixing of the oxides and sintering them pellets can be obtained, which are well homogeneous as regard their oxygen to metal ratio.

It should be remarked that the value of M used in eq. I depends on z. An equation for  $\Delta [O/M]$  caused by variations in M is

$$\frac{\Delta [O/M]}{2 - [O/M]} = \frac{\Delta M}{M} \quad (\text{VIII})$$

By substitution of extreme values in eq. VIII ( $\Delta M = 1$ ,  $M = 270$ ,  $[O/M] = 180$ ) a value of  $7.4 \cdot 10^{-4}$  is found for  $\Delta [O/M]$ , indicating that in any case this effect can be neglected.

The second possibility concerns non-uniformly distributed impurities. In this case three different equations relate  $\Delta [O/M]$  to the quantity of impurities:

a) for chemically inert impurities

$$\Delta [O/M] = 0.01 P ([O/M]^{-2}) \quad (\text{IX})$$

where P = percentage of impurities after equilibration

b) for impurities which undergo oxidation-reduction reaction during the equilibration of the sample with the carbon monoxide - carbon dioxide mixture at 850°C:

$$\Delta [O/M] = 0.01 P \left( [O/M]^{-2} \pm \frac{270}{M_i} v \right) \quad (\text{X})$$

where  $M_i$  = molecular weight of the impurity after equilibration,  $MO_y$ , obtained by the reaction  $MO_{y+v} \xrightleftharpoons[\text{ox}]{\text{red}} MO_y$ .

P = percentage of impurities after equilibration

Values of  $\frac{270 v}{M_i}$  are found to vary between 1.5 and 7.5

From equation X it can be derived that the amount of impurities normally present in plutonium and uranium oxides ( $< 1000$  ppm) will hardly influence the precision of the determination. However, extreme care should be taken as not to contaminate the samples with non-uniformly distributed impurities. From equation X it follows that the presence of quantities of 40  $\mu$ g of aluminium metal or 75  $\mu$ g of chromium metal in a 200 mg sample and their absence in another one may cause a  $\Delta [O/M]$  of 0.003 between the results obtained with these samples.

c) for volatile impurities including organic substances:

$$O/M = 0.168 P' \quad (XI)$$

where  $P'$  = percentage of impurities before equilibration

It is easily seen that the limit of interference decreases in the order in which the three types are listed.

In order to answer the question what substances might interfere according to equations IX and X the integral free energy values per mole of oxygen were calculated for the reduction of a valency state to the next lower valency state for a series of elements. The integral values found are given in fig. 5 A and B, in which the  $\Delta G$ -value for the carbon monoxide - carbon dioxide mixture (10 + 1) at 850°C is also indicated. The oxidation state of each element after equilibration corresponds to the first level above the line for the carbon monoxide - carbon dioxide mixture, or -- in the absence of such a level - to the metallic state. From fig. 5 A and B the following conclusions can be drawn.

a) the following elements if present in the metallic state, are oxidized under the conditions of the determination:

Be, Mg, Ca, Sr, Ba, Al, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mn, Si, Ce, Nd, Sm, Th,

b) the following elements and compounds are volatilized under the conditions of the determination:

Zn, Cd, Pb, Bi,  $V_2O_5$ ,  $MoO_3$ ,  $RuO_4$ ,  $PbO$ .

c) the oxides of the following elements are reduced to the metallic state:

Mo, W, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, In, Pt, Cu, Ag, Au, Cd, Sn, Pb, Bi.

d) the following oxides are reduced to lower oxides:

$TiO_2$ ,  $VO_2$ ,  $Mn_3O_4$ ,  $CeO_2$ ,  $PrO_2$ .

Consequently the following oxides do not undergo any change and interfere only according to eq. IX

$BeO$ ,  $MgO$ ,  $CaO$ ,  $SrO$ ,  $BaO$ ,  $Al_2O_3$ ,  $Y_2O_3$ ,  $ZrO_2$ ,  $HfO_2$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $Cr_2O_3$ ,  $SiO_2$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $ThO_2$ .

The same conclusion is valid for the following metals:

Mo, W, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, In, Pt, Cu, Ag, Au, Sn.

It has experimentally been verified that Co, Fe and W are not oxidized under the conditions of the determination, whereas Cr and Zr are oxidized to  $CrO_{2.98}$  and  $ZrO_{1.98}$  respectively. The Ce-oxide which is in equilibrium with the carbon monoxide - carbon dioxide atmosphere has the composition  $CeO_{1.7}$ .

It is evident that the elements, mentioned above, do not only influence the precision when they are distributed non-uniformly within samples, but they also influence the accuracy, even when they are distributed quite uniformly.

The next remark concerns the correction for the water content. When the water content of the sample would imply a correction in the oxygen to metal ratio of less than the standard deviation for homogeneous samples (0.0010), it can be neglected. This is very often the case with sintered pellets which usually contain less than 60 ppm of water, the quantity which corresponds to 0.0010 in the oxygen to metal ratio.

Concerning the time required for analysis it should be noted that 4 1/2 hours are required to weigh and handle six samples to be equilibrated together. So, one operator can handle an average of ten to twelve samples per day provided that the capacity of the apparatus is large enough.

The method investigated compares favourably with other methods. For the gravimetric method using a thermobalance, a standard deviation of a single determination of 0.004 has been reported (6.9). This method has the advantage of less complicated manipulations and the disadvantage that only one sample can be handled at a time.

MARKIN and BONES (6.10) report a standard deviation of 0.00013 of a single determination using the coulometric titration method, developed by these authors. The method was applied to a sample of slightly overstoichiometric uranium dioxide. However, for the analysis of large series of samples the method seems to be less suited than the gravimetric method, since the manipulations involved are more complicated.

## 6. Conclusions

1. It is advisable to pass the CO/CO<sub>2</sub>-mixture over copper at 600°C before it is allowed to react with the mixed oxide to be equilibrated in order to decompose iron carbonyls.
2. An influence of the composition of the sample (plutonium oxide, mixed oxides) on the precision of the results cannot be detected.
3. The most precise results are obtained when a microbalance is used.
4. Using a microbalance, simultaneous weighing of a reference weight is indispensable.
5. In the microprocedure the standard deviation decreases with increasing sample size. Maximum precision is obtained with samples of at least 200 mg.
6. The standard deviation of a single determination of the O/M ratio according to the microprocedure on a sufficiently homogeneous sample is 0.0010.
7. Part of the dispersion found with normal samples using a microbalance is due to sample inhomogeneities.
8. Samples, duplicate results from which differ more than 0.0033, are to be considered as inhomogeneous.

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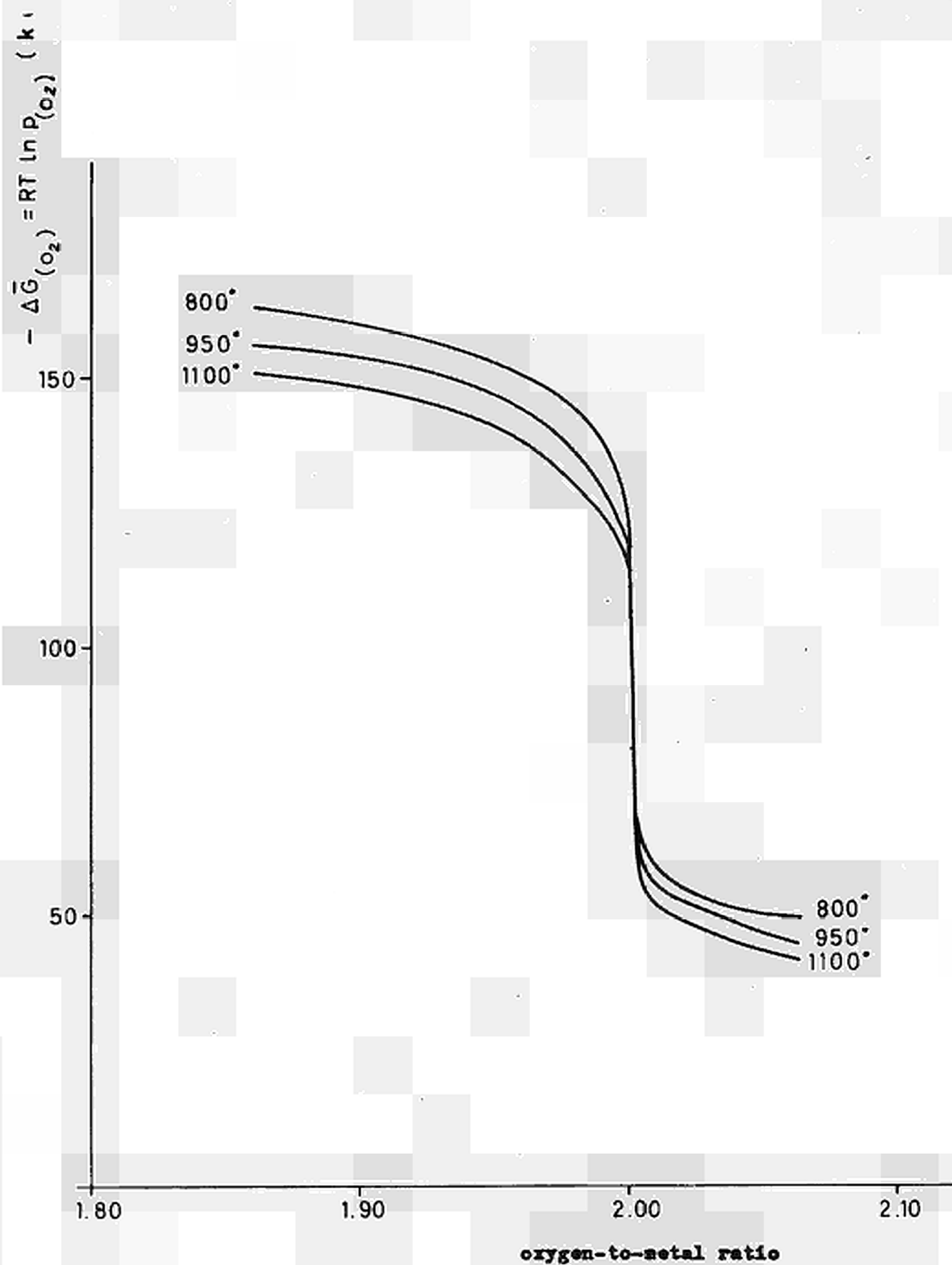


Fig. 1 -  $\Delta\bar{G}_{(O_2)}$  versus oxygen to metal ratio for  $U_{0.7}Pu_{0.3}O_{2+x}$  (6.3)

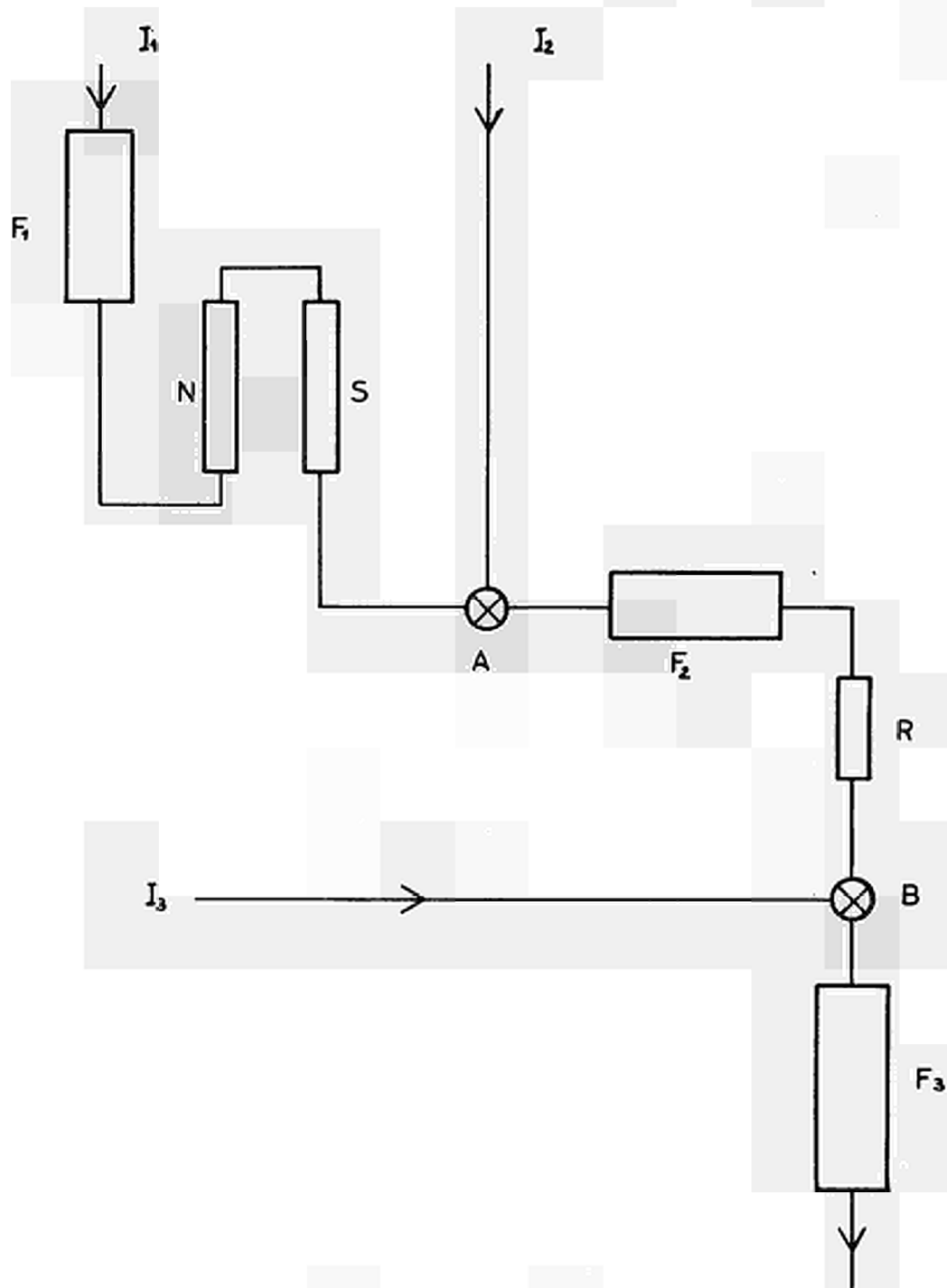
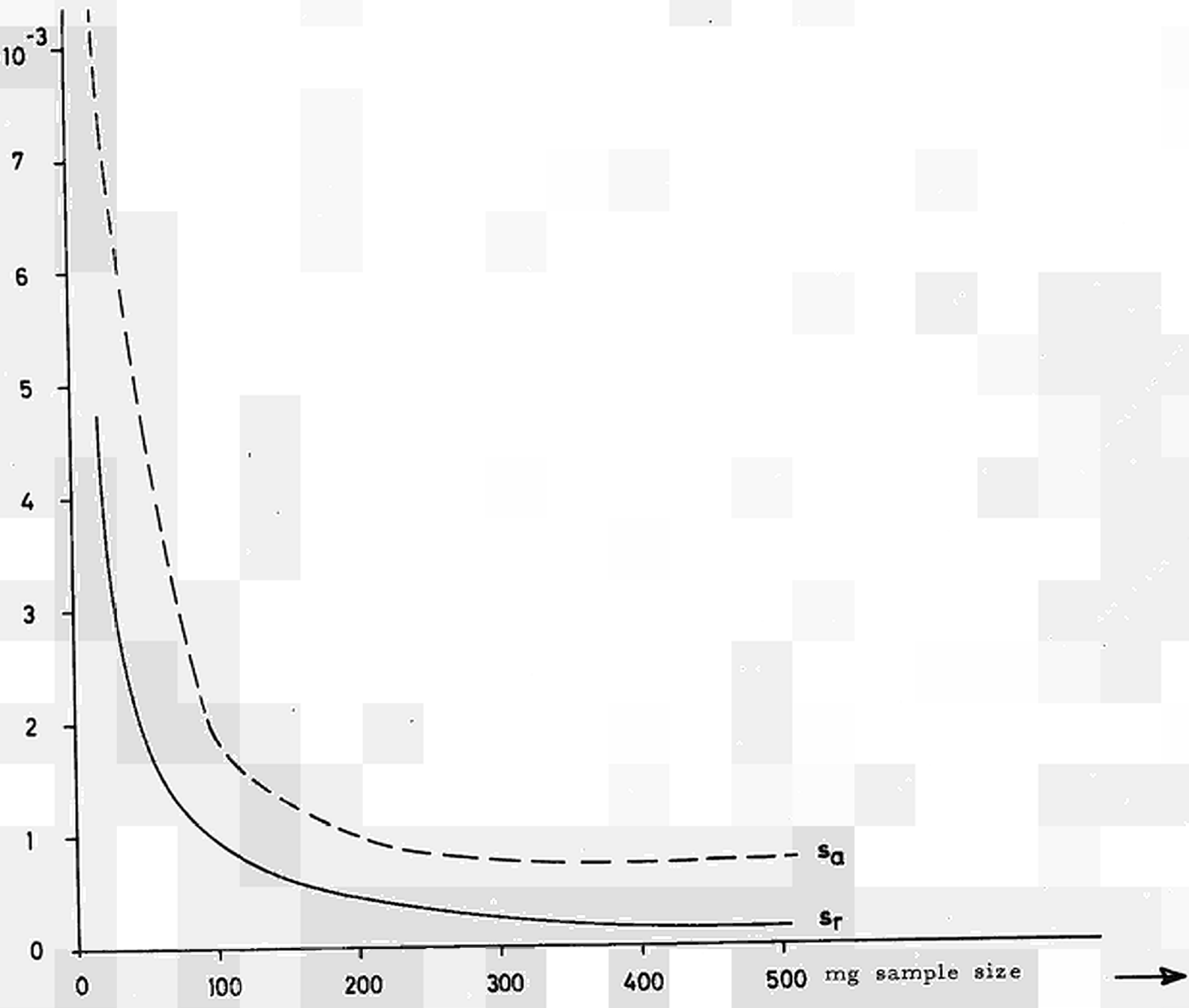


Fig. 2

Scheme of the installation for the determination of the oxygen to metal ratio.

A and B : stop cocks  
 F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub>: furnaces  
 N : column filled with NaOH pellets  
 S : column filled with silicagel and molecular sieves  
 I<sub>1</sub> : argon inlet  
 I<sub>2</sub> : CO/CO<sub>2</sub> inlet  
 I<sub>3</sub> : air inlet  
 R : rotameter

standard deviation  $8 \cdot 10^{-3}$



**Fig. 3**  
Theoretical ( $s_r$ ) and experimental ( $s_a$ ) precision as a function of the sample size

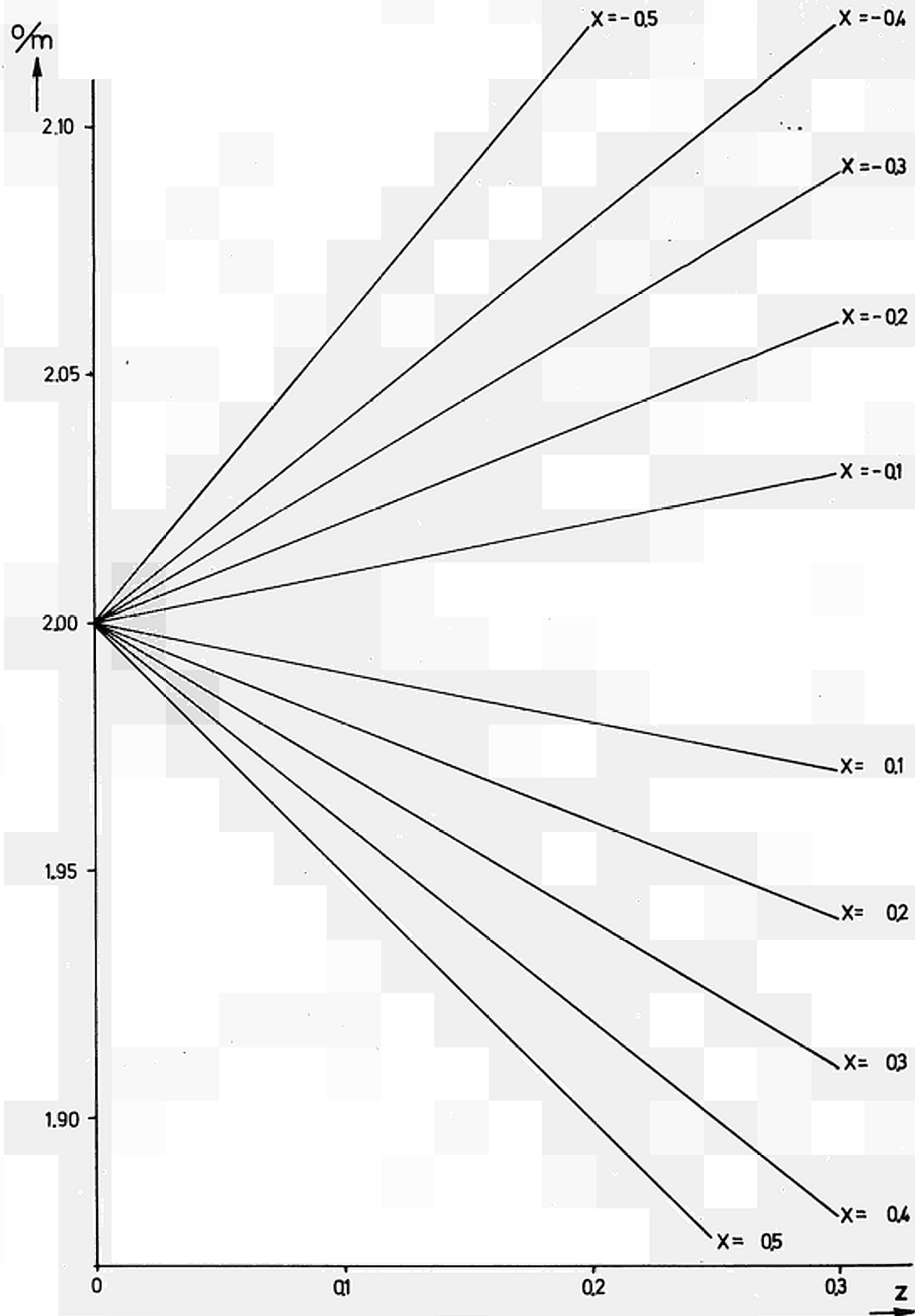


Fig. 4

The oxygen to metal ratio  $O/M$  as function of  $z$  for different values of  $x$

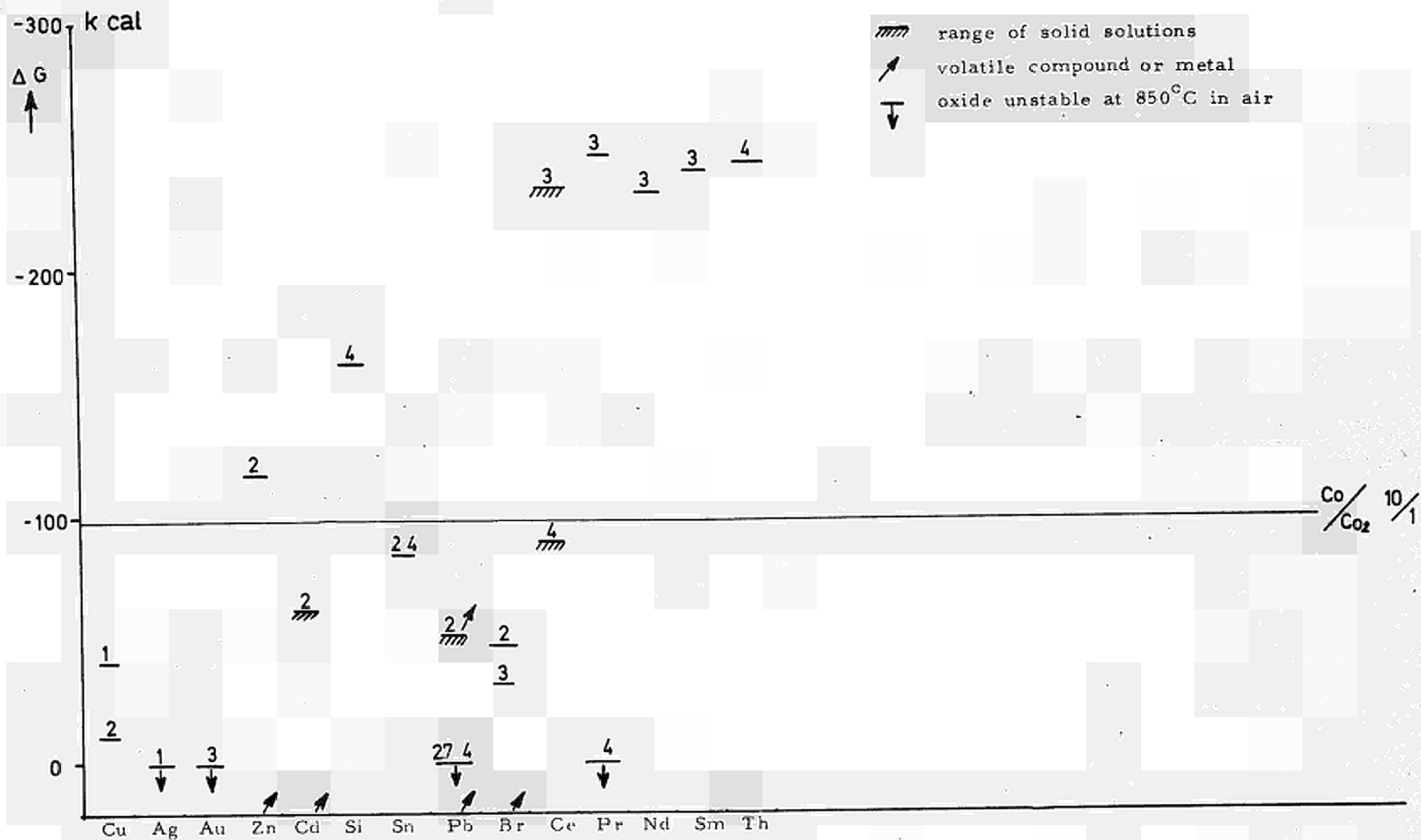


Fig. 5 B

Integral free energy changes for reactions  $\frac{2}{y} \text{MO}_{x \cdot y} \longrightarrow \frac{2}{y} \text{MO}_{x-y} + \text{O}_2$  (2 x irradiated above horizontal bars)

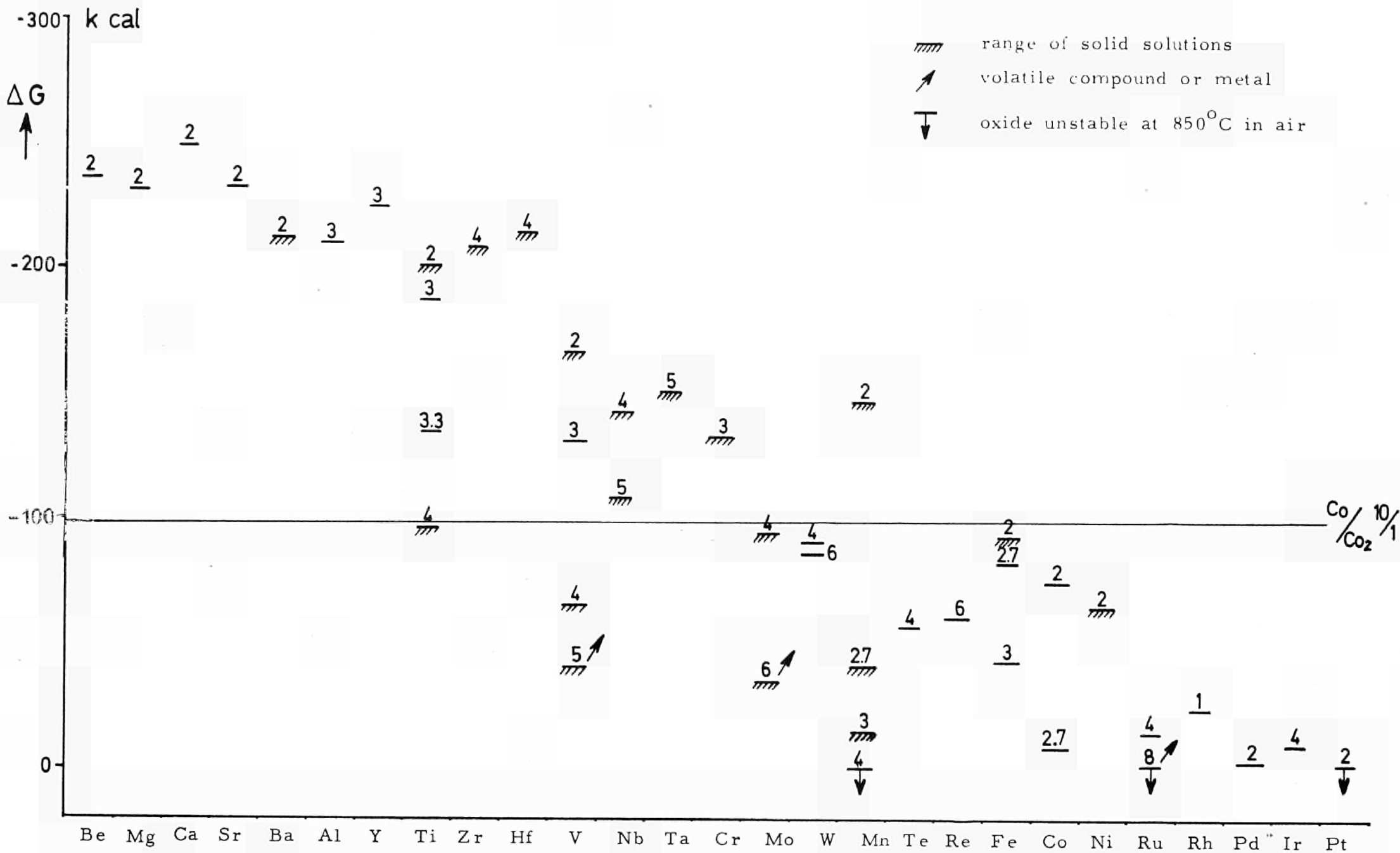


Fig. 5 A

Integral free energy changes for reactions  $\frac{2}{y} \text{MO}_x \rightarrow \frac{2}{y} \text{MO}_{x-y} + \text{O}_2$  (2 x irradiated above horizontal bars)

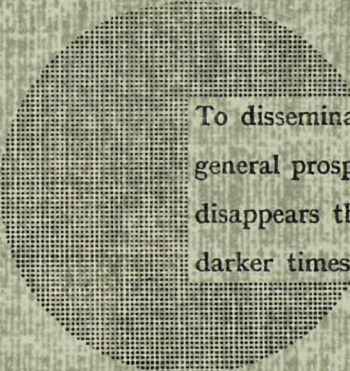
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Alfred Nobel

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