

traces go direct to the leaves in the young stage (L. N. Rao, 1972). The course of leaf bundles in the cortex is direct in Cycadofilicales and Bennettitales, while most of the Cycads are characterized by the girdling of the bundles. Consequently Cycads like some species of Macrozamia which show a direct course of the bundle in the adult plant, and Bowenia which show a similar arrangement in the seedling, are nearer the fern condition in this respect (Chamberlain, 1919). Since *C. circinalis* and *C. beddomei* have direct course of the leaf trace bundles both in the young and old stages, they should represent a condition near to the fern condition. During the course of investigation nowhere has the girdle trace been noticed.

#### DISCUSSION

According to Foster and Gifford (1958) the course of vascular bundle which supply each leaf is complex. Since the various strands entering a given leaf extend horizontally through the cortex before entering the leaf base, a girdling arrangement is seen in a thick and cleared section of the stem. The xylem is traversed by numerous broad parenchymatous rays. It is the *Zamia floridana* transverse section of the stem first published in a textbook of Botany by Coulter, Barnes and Cowles (1910) that has given the idea of the leaf-girdle. The leaf trace after emerging out of this vascular cylinder bifurcates and each part goes round the central vascular cylinder to meet at the opposite side and enter the leaf at a higher level. This idea got wide publicity in the early twenties and continues even today since the *Cycas* anatomy has

not been worked out for any species of *Cycas*. It is taken for granted that what is found in *Zamia* is also found in *Cycas* which is not true. The girdling though common to other Cycadeales is not to be found in some Cycads like some species of macrozamia (Chamberlain, 1919). *Cycas circinalis* and *C. beddomei* Dyer. also fall under this class. They do not have leaf trace girdles and come very near Cycadofilicales. If such bundles as occur in leaf traces, leaves, peduncles and cotyledon were present in the primary cylinder, it would correspond to that of Lyginodendron (Coulter and Chamberlain, 1910). All the above characters are primitive ones and hence take the *Cycas* very near their ancestors.

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## ON THE KINETICS OF FORMATION OF A 8 Cu-3 Ni ALLOY BY THE $\text{Ni}_3\text{S}_2\text{-Cu}_2\text{O}$ REACTION UNDER REDUCED PRESSURE

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#### ABSTRACT

The kinetics of the reaction between  $\text{Ni}_3\text{S}_2$  (l) and  $\text{Cu}_2\text{O}$  (s) resulting in the formation of a 8 Cu-3 Ni alloy have been investigated in the temperature range 850–1050° C under reduced pressure ( $\sim 0.05$  mm Hg). The reaction has been found to be rapid in the initial stages and subsequently progresses in accordance with a parabolic rate law (from  $\sim 30$  to  $\sim 85\%$  reduction). Possible mechanisms have been suggested.

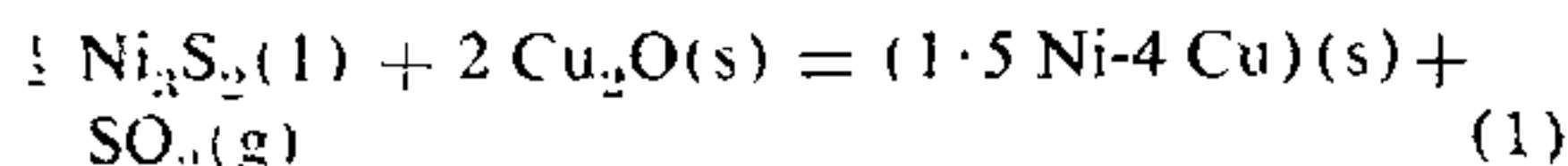
#### INTRODUCTION

THE reactions between sulphides and oxides of different metals as means of preparing alloys have received very little attention of metallurgists. In the blowing of nickel matte to produce  $\text{Ni}_3\text{S}_2$ ,

besides the  $\text{Ni}_3\text{S}_2\text{-NiO}$  reaction, the  $\text{Ni}_3\text{S}_2\text{-Cu}_2\text{O}$  reaction<sup>1</sup> is also considered to take place resulting in the formation of a small proportion of Cu-Ni alloy. Four decades ago Tafel and Klewata<sup>2</sup>, who investigated the reaction between  $\text{Cu}_2\text{S}$  and  $\text{NiO}$ ,

stated that the reaction is thermodynamically feasible above 1330° C. Recently, Prasad and Jena<sup>3</sup> were successful in preparing a 1:1 Cu-Ni alloy by the  $\text{Cu}_2\text{S}$ -NiO reaction under reduced pressure. The present work is concerned with a study on the kinetics of formation of a 8 Cu-3 Ni alloy by the  $\text{Ni}_3\text{S}_2$ - $\text{Cu}_2\text{O}$  reaction.

The variation of standard free energy of formation with temperature for the reaction:



has been calculated (from the recent thermodynamic data)<sup>4-6</sup> to be

$$\Delta G^\circ = 22370 - 25.54 T \quad (800 \text{ to } 1100^\circ \text{ C}).$$

Under standard conditions, the reaction is thermodynamically feasible at 603° C and may take place at a much lower temperature under reduced pressure. Thermal dissociations of  $\text{Ni}_3\text{S}_2$  and  $\text{Cu}_2\text{O}$  leading to the formation of the concerned metals (and hence the alloy) do not appear thermodynamically feasible below 3370° and 2075° C, respectively, under standard conditions. Thus the sulphide-oxide reaction appears to be very much more thermodynamically feasible than the dissociation reactions. Preliminary studies showed that  $\text{Ni}_3\text{S}_2$  as well as  $\text{Cu}_2\text{O}$  were unaffected even by heating upto 1150° C under reduced pressure ( $\sim 0.05$  mm Hg), whereas the  $\text{Ni}_3\text{S}_2$ - $\text{Cu}_2\text{O}$  reaction took place to a considerable extent by treatment even at 900° C for a few minutes under the same reduced pressure.

#### EXPERIMENTAL

$\text{Ni}_3\text{S}_2$  required for the investigation was prepared by the thermal dissociation of freshly precipitated nickel sulphide as described elsewhere<sup>7</sup>. The lustrous sulphide ( $-65$  mesh) was of 99.8% purity.  $\text{Cu}_2\text{O}$  ( $-100$  mesh) was prepared by the thermal dissociation of cupric oxide (E. Merck) at 1100° C under reduced pressure ( $\sim 0.05$  mm Hg) for 2 hrs. The brick red oxide had a purity of 99.9%.

The experimental set-up and procedure employed for the kinetic study were essentially similar to those employed by Prasad and Jena<sup>7</sup> in their studies on the  $\text{Ni}_3\text{S}_2$ -NiO reaction. Isothermal weight loss measurements were taken on 2 gm samples of the sulphide-oxide mixture at different temperatures (850–1050° C) for chosen times (5 mins—several hrs) under a reduced pressure of  $\sim 0.05$  mm Hg. As sulphur dioxide is the only gaseous product, the progress of the reaction was followed by the said weight loss measurements and the mole per cent reacted of either constituent readily calculated.

#### RESULTS AND DISCUSSION

Results obtained on the kinetics of  $\text{Ni}_3\text{S}_2(l)$ - $\text{Cu}_2\text{O}(s)$  reaction at 850°, 900°, 950°, 1000° and 1050° C under reduced pressure are presented in Fig. 1. From these mole % reacted (N) vs time

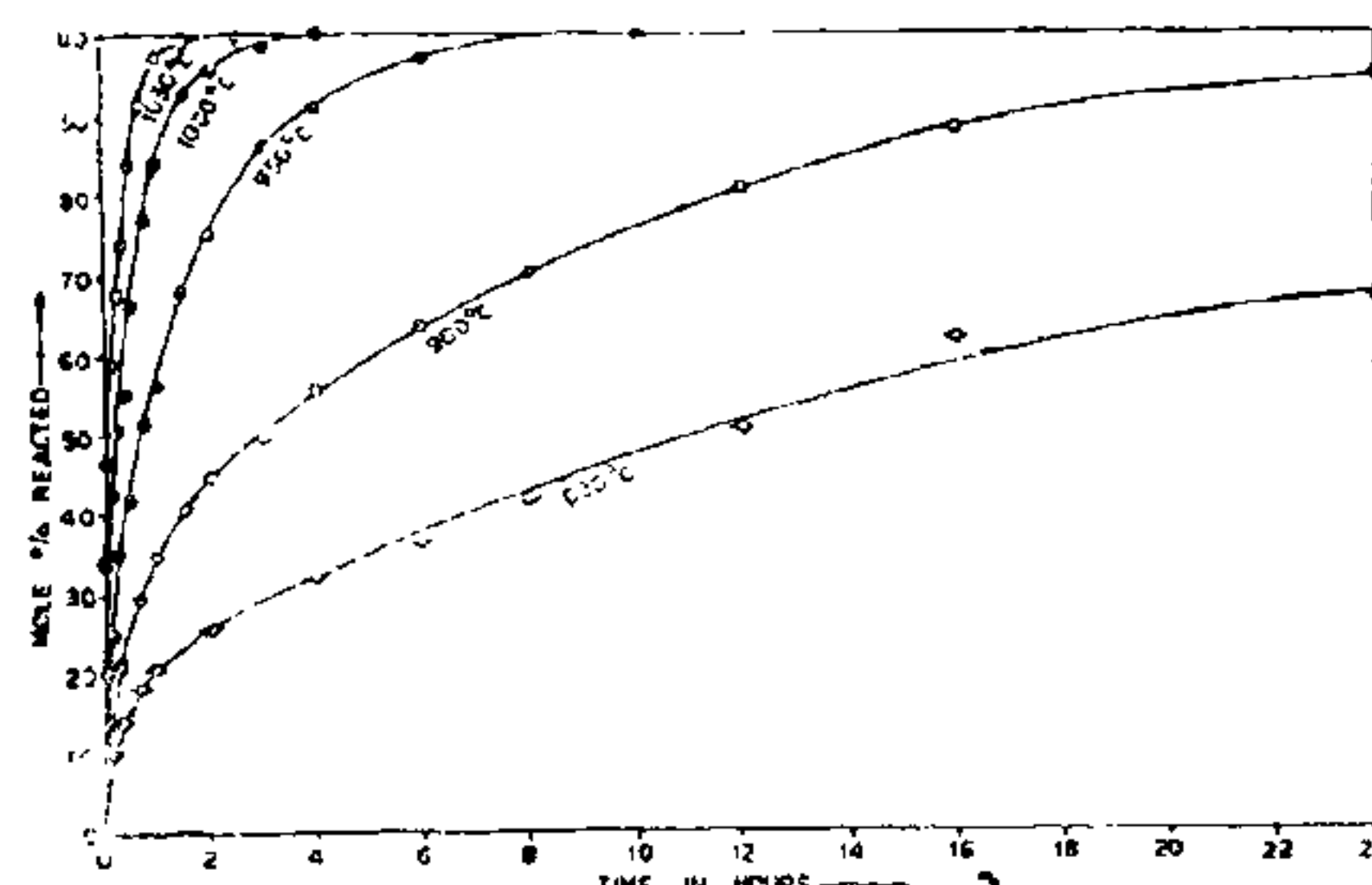


FIG. 1. Progress of  $\text{Ni}_3\text{S}_2(l)$ - $\text{Cu}_2\text{O}(s)$  Reaction at various temperatures.

( $t$ ) plots, the marked influence of temperature on the amount reacted at any time is self evident. In general, the reaction has been found to be very rapid in the initial period and slow down with increase in time. From the limited results available at 850°, 900°, and 950°, activation energy for the first 10% reaction has been calculated, to be approximately 38 kcal/mole.

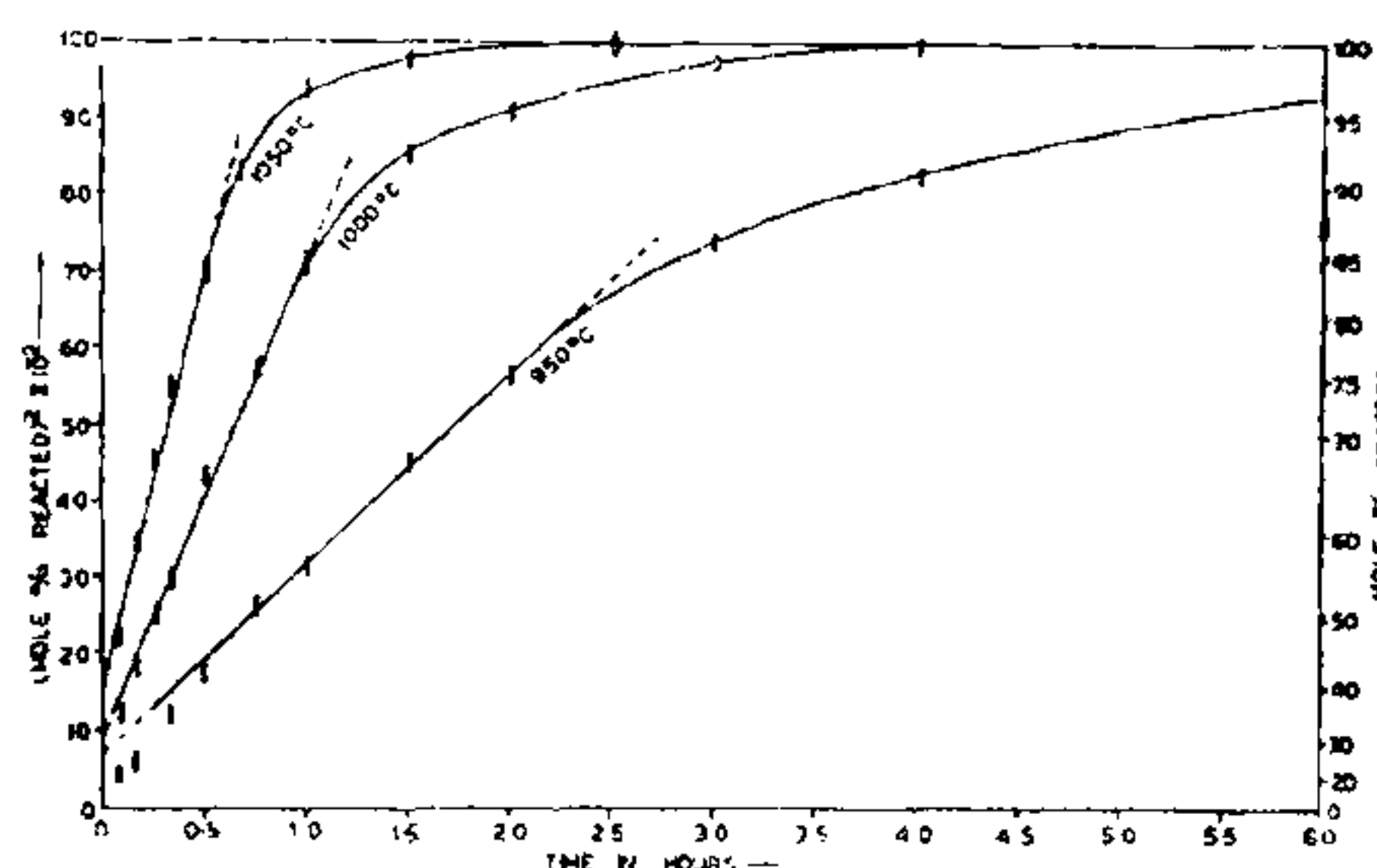


FIG. 2 A.  $(\text{Mole \% reacted})^2$  vs time plots at higher temperatures.

The  $N^2$  vs  $t$  plots, shown in Figs. 2 A and 2 B, reveal that the reaction progresses in accordance with a parabolic rate law, i.e.,  $N^2 = k_p t + C$  (where  $k_p$  represents the parabolic rate constant) from about 30% to about 85% reduction at all the temperatures of study. Values of the slopes of the linear region of the  $N^2$  vs  $t$  plots were taken at various temperatures. The  $\log k_p$  values, thus obtained, are seen to vary linearly with  $1/T^\circ \text{K}$  (Fig. 3). From the slope of this Arrhenius plot, activation energy for this parabolic stage of the  $\text{Ni}_3\text{S}_2$ - $\text{Cu}_2\text{O}$  reaction has been calculated to be



$63 \pm 4$  kcal/mole. The reaction has been found to be very sluggish beyond about 85% reduction at all the temperatures of study.

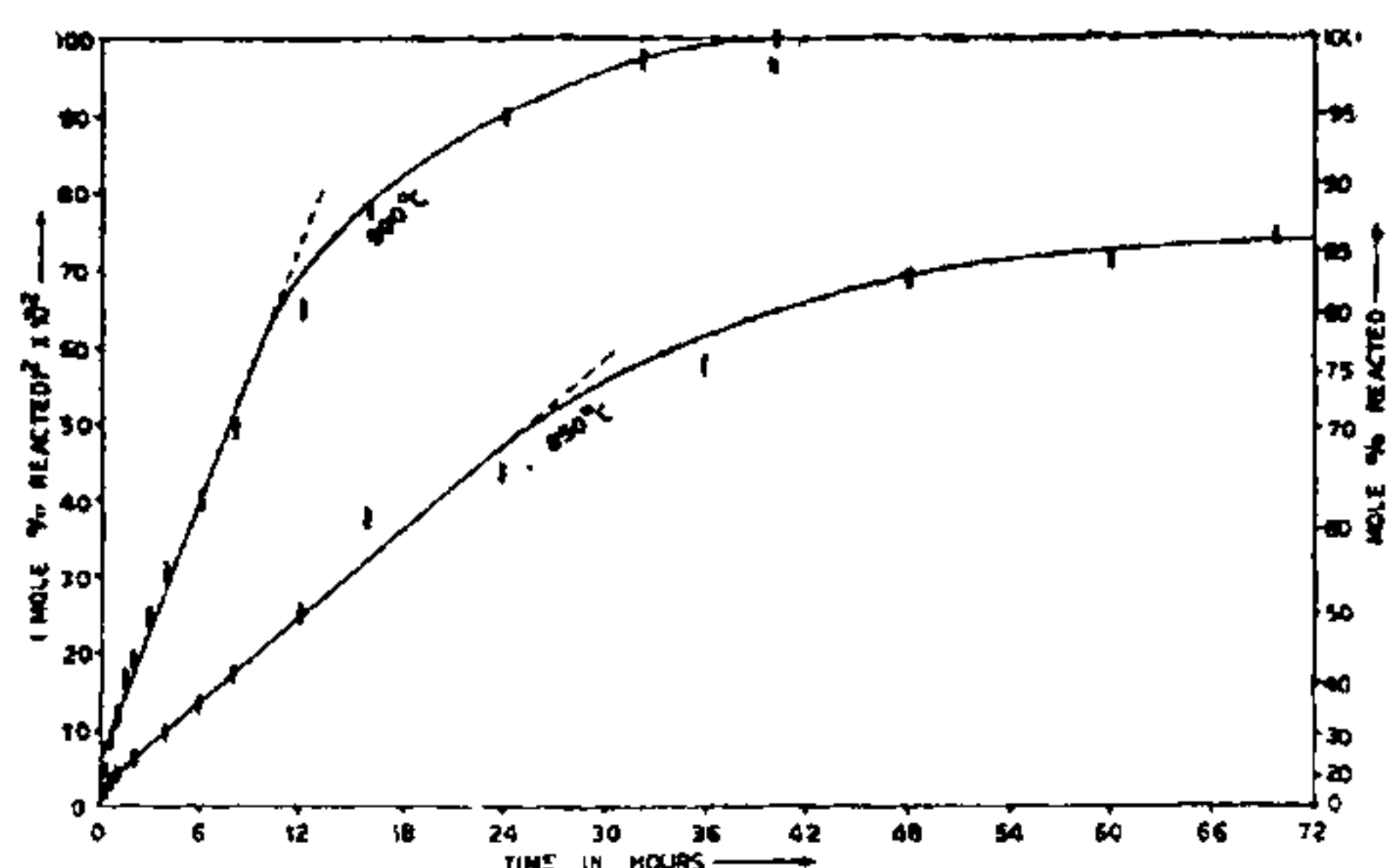


FIG. 2 B. (Mole % reacted)<sup>2</sup> vs time plots at lower temperatures.

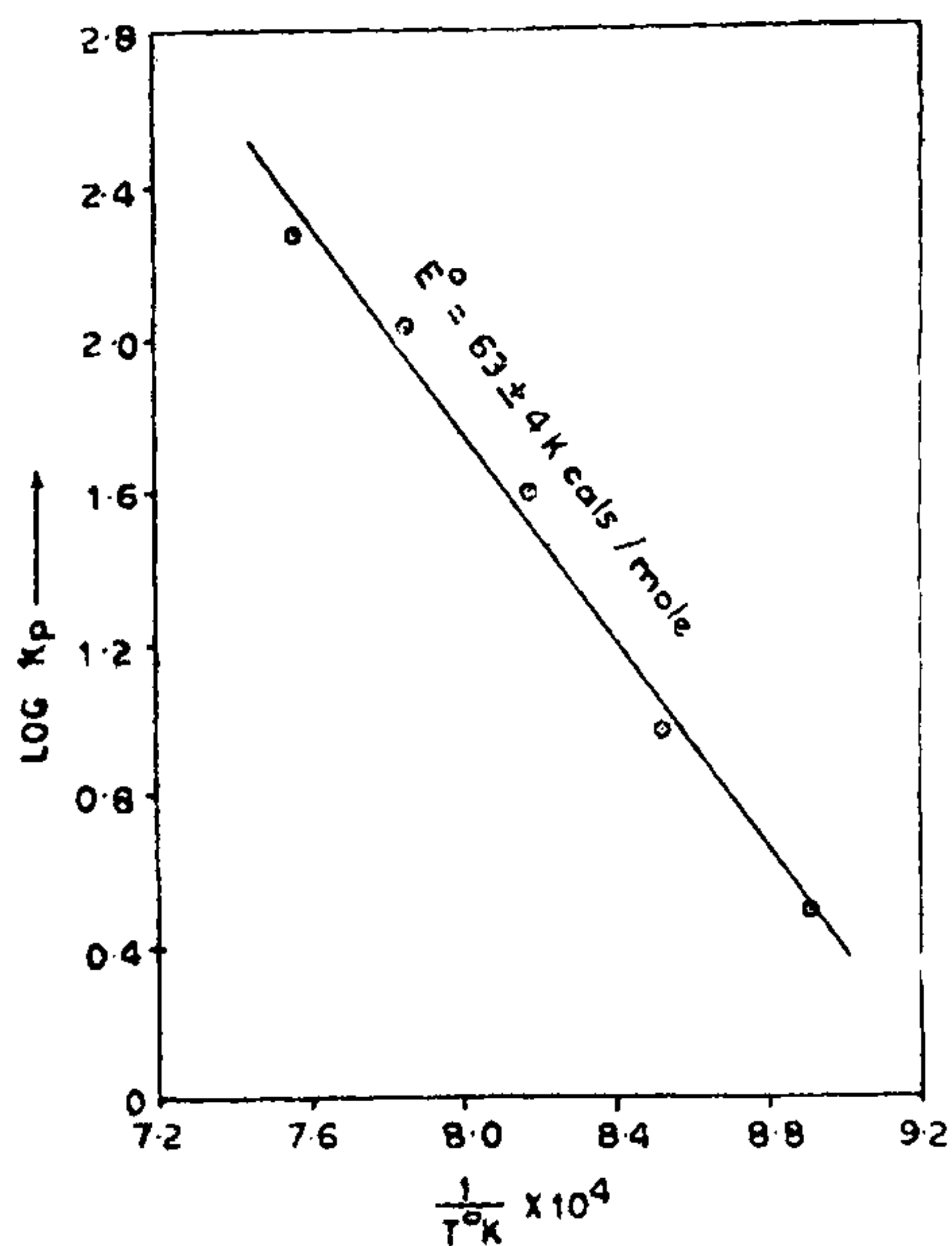
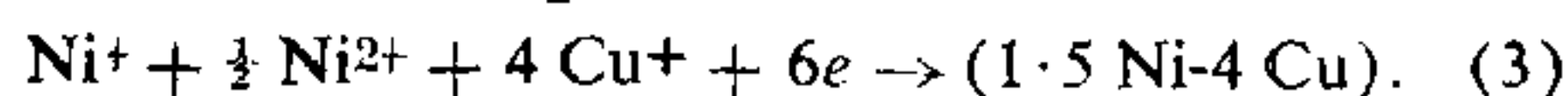


FIG. 3. Activation energy plot.

It is relevant to mention here that similar results have been reported in the case of a few other sulphide-oxide reactions also. The  $\text{Cu}_2\text{S}-\text{NiO}^7$ ,  $\text{Ni}_3\text{S}_2-\text{NiO}^7$  and  $\text{Co}_4\text{S}_3-\text{NiO}^8$  reactions have been found to be initially rapid, and progress subsequently in accordance with a parabolic rate law and finally at a very sluggish rate.

The reaction between  $\text{Ni}_3\text{S}_2$  (m.p.  $810^\circ\text{C}$ ) and  $\text{Cu}_2\text{O}$  (m.p.  $1230^\circ\text{C}$ ) is quite complex and may be considered to proceed in the following manner:

As soon as the  $\text{Ni}_3\text{S}_2-\text{Cu}_2\text{O}$  mixture is heated, the reaction will be initiated at the interface of the reactants and the Cu-Ni alloy can be formed according to the reactions



The occurrence of the reaction (2) may be initially accompanied by the formation of a cation- and electron-excess  $\text{Ni}_3\text{S}_2$  and  $\text{Cu}_2\text{O}$ ; and subsequent migration of these cations and electrons may then take place to suitable nuclei followed by their discharge on these nuclei similar to the model suggested by Wagner in his study on the  $\text{Cu}_2\text{S}-\text{Cu}_2\text{O}$  reaction<sup>9</sup>. These nuclei may be assumed to be available at the interface itself, where the chances of supersaturation of the reactants (and hence precipitation) are a maximum\*. The Cu-Ni alloy formed may be held in solution in the reactants (particularly in the liquid  $\text{Ni}_3\text{S}_2$ ) until its solubility limit is reached. Beyond this solubility limit a layer of Cu-Ni alloy may be formed at the interface of the reactants. Once this barrier is formed the reaction rate may be governed by (i) diffusion of  $\text{O}^{2-}$  through the alloy barrier and subsequent reaction at the alloy/sulphide interface and/or (ii) diffusion of  $\text{S}^{2-}$  through the alloy barrier and subsequent reaction at the alloy/oxide interface.

The above model visualizes two distinct stages in the reaction, viz., the initial stage (surface reaction) culminating in the formation of the alloy barrier and a subsequent stage governed by the diffusion across this alloy layer. Experimental observations, discussed earlier, show that the reaction takes place in two stages with two very different activation energies: (i) an initially rapid reaction with a comparatively low activation energy (ii) a subsequently slow reaction in accordance with a parabolic rate law (which is indicative of diffusion control) with a relatively high activation energy.

It is interesting to note here that the activation energy value observed in the present study for the initial stages of the  $\text{Ni}_3\text{S}_2-\text{Cu}_2\text{O}$  ( $\sim 38$  kcal/mole) is not very different from the activation energy values reported for the initial stages of the  $\text{Ni}_3\text{S}_2-\text{NiO}$  ( $\sim 45$  kcal/mole<sup>7</sup>) and  $\text{Co}_4\text{S}_3-\text{CoO}$  ( $\sim 40$  kcal/mole<sup>10</sup>) reactions investigated under similar experimental conditions. This observation leads one to believe that in all these sulphide-oxide

\* Since Cu and Ni are fully miscible in each other and these atoms are formed simultaneously *in situ*, the alloy formation is considered to be a relatively easy process.

reactions, the same surface reaction controls the rate of the initial stage.

As far as the subsequent parabolic stage of the reaction is concerned, its rate may be determined by the diffusion of  $O^{2-}$  and/or  $S^{2-}$  in the alloy layer. Lack of data on the Ni-S-O-Cu phase diagram and diffusivities of  $O^{2-}$  and  $S^{2-}$  in the 8 Cu-3 Ni alloy places a limitation in understanding the exact rate determining step(s).

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## $\delta(O^{18})_{\text{WHOLE ROCK}}$ FROM $\delta(O^{18})_{\text{QUARTZ}}$ AND ITS PETROGENETIC SIGNIFICANCE

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#### ABSTRACT

In felsic plutonic igneous rocks and metamorphic rocks,  $\delta(O^{18})_{\text{quartz}}$  (X) can be related to  $\delta(O^{18})_{\text{whole rock}}$  (Y) by the equation  $Y_x = 0.8237 X + 0.36$ . In basic plutonic igneous rocks and eclogites, the relationship is  $Y_x = 1.037 X - 3.328$ . The two equations enable computation of  $\delta(O^{18})_{\text{whole rock}}$  from experimentally measured  $\delta(O^{18})_{\text{quartz}}$  values, within  $\pm 1.2$  permil and  $\pm 0.5$  permil, for the two rock groups, respectively, at the 95% confidence level. The computed  $\delta(O^{18})_{\text{whole rock}}$  values can be used to evaluate the roles of specific petrological processes in the evolution of granitic bodies.

#### INTRODUCTION

RECENT investigations by the author have highlighted the significance of  $\delta(O^{18})_{\text{quartz}}$  in problems of granite petrogenesis. Some of the results reported show that  $\delta(O^{18})_{\text{quartz}}$  is a potentially useful isotopic tracer to determine if a granitic pluton is of magmatic or metasomatic origin<sup>1</sup>. The need for applying oxygen isotope techniques to problems of igneous and metamorphic rock complexes in India (e.g., granitic, migmatitic, charnockitic, khondalitic, alkaline, carbonatitic) has been emphasised by the author elsewhere<sup>2</sup>. The object of the present paper is twofold: first, to propose two curves and equations for computing  $\delta(O^{18})_{\text{whole rock}}$  from experimentally measured values of  $\delta(O^{18})_{\text{quartz}}$ , one applicable to felsic plutonic igneous rocks and metamorphic rocks, and the other to basic plutonic igneous rocks and eclogites; and second, to discuss briefly, the petro-

genetic significance of  $\delta(O^{18})_{\text{whole rock}}$  in granite studies.

#### NOTATION

Oxygen is a mixture of three stable isotopes, of atomic weights 16, 17 and 18<sup>3,4</sup>. The abundances of these three isotopes in air<sup>5</sup> are  $O^{16} = 99.7587$ ;  $O^{17} = 0.0374$ ;  $O^{18} = 0.2039$ . All oxygen-bearing rock-forming minerals contain  $O^{18}$  and  $O^{16}$ ; any possible enrichment of the heavier isotopes is assumed to be due to  $O^{18}$  because of the very low abundance of  $O^{17}$ . Data on oxygen isotope fractionation of unknown samples are usually reported as deviations of the  $O^{18}/O^{16}$  ratio, in parts per thousand (‰ or permil), from the same ratio in an arbitrary standard. The reference standard, in modern investigations, is "Standard Mean Ocean Water" or "SMOW"<sup>6</sup>. The results are presented according to the formula<sup>7</sup>:

$$\delta O^{18} = \left[ \frac{(O^{18}/O^{16})_{\text{sample}}}{(O^{18}/O^{16})_{\text{standard}}} - 1 \right] 1000,$$