SEMIANNUAL REPORT

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INTRODUCTION

It was stated in the first semi-annual report (dated October, 1967) that even though the tektites usually possess a high degree of homogeneity, definite indications of the presence of striations can be observed when a tektite specimen is examined under a microprobe.

The tektite can, therefore, be considered as an aggregate of diffusion couples with some unknown initial conditions that have experienced a diffusion anneal. Both the initial conditions and the thermal history depend upon the origin of the tektite.

It is our attempt to estimate the thermal history of the tektite through the following experiments:

(i) Obtain electron microprobe analyses of the concentration distribution of certain elements in an "as recovered" tektite along known directions.

(ii) Set up a diffusion equation describing the diffusive mixing of those elements and hence calculate the diffusion-time product, $D_{im} \cdot t$, where

D_{im} = effective binary diffusion coefficient

t = diffusion time

(iii) Obtain the effective binary diffusion coefficient, D_{im}, by an interdiffusion experiment consisting of synthetic glasses around the tektite composition.

The data on D_{im} measurements is to be supplemented with the data of self diffusion coefficients, D_i.

In the first semi-annual report, some measurements of the concentration distribution of various elements in an as-recovered tektite were reported. In the second period, emphasis was concentrated on measurements in K_2O-SrO-SiO_2 glass and in the understanding of effective binary diffusion coefficients in multicomponent systems. Efforts during the past six months have primarily been directed towards the techniques of measurement of D_{im} in synthetic tektite glasses.

MELTING OF TEKTITE GLASSES

Attempts were made to melt homogeneous, bubble-free glasses simulating a tektite composition. Only major constituents were included because it was assumed that the omission of the minor constituents

would not greatly change the diffusion phenomena whereas at the same time the kinetics of the mixing process would be easier to study because of lesser number of species.

Table I lists compositions A, B and C which have been melted with the intent of measuring the effective binary diffusion coefficient of Fe in particular.

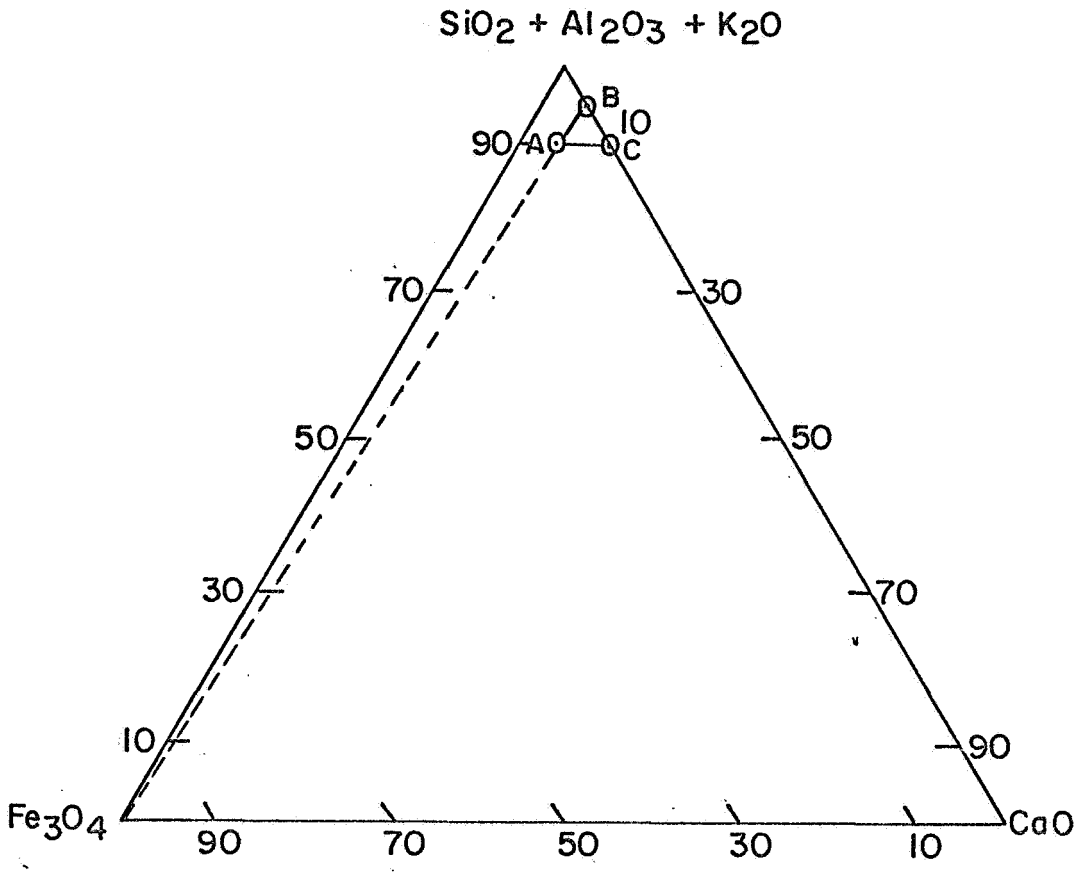
TABLE I

Weight Per Cent Compositions of the Glasses Used

	Glass A	Glass B	Glass C	Raw Material
SiO_2	72.0	76.2	72.1	SiO_2
Al_2O_3	13.0	13.75	13.1	Al_2O_3
CaO	5.5	5.8	10.7	$CaCO_3$
Fe_3O_4	5.5	--	--	Fe_3O_4
K_2O	4.0	4.25	4.08	K_2CO_3

Figure 1 is a ternary composition space where SiO_2, Al_2O_3 and K_2O have been put together as one component, the other two being CaO and Fe_3O_4. It is clear that the glass A and B are suitable end members for the determination of the true D_{FeM}.

FIG. 1



The raw materials were finely powdered analytical reagents. Approximately 500 g of the batch was weighed out and thoroughly mixed. Melting was carried out in a silica crucible inside a "globar" resistor furnace at 1550°C for periods ranging from about 15 hours to as much as 150 hours.

It was observed that even at 1550°C, all the glasses were very viscous. Although a 60 hours melt of glass A was reasonably seed free, glass B contained undissolved particles, even after 150 hours of melting.

The low degree of attack of the glasses on the silica crucible was particularly striking. Very little adhesion of the glass to the crucible was found, and as a result the crucible could be chipped away with relative ease.

Remelting of the glasses, particularly the composition B, was carried out at higher temperatures. Fragments of the pre-melted glass were kept inside a calcia stabilized ZrO_2 crucible and were heated to a maximum temperature of about 1800°C (soaking time at 1800°C $\sim$ 4 hours) in a gas fired furnace.

While glasses A and C appeared to be very homogeneous and virtually seed free, glass B still contained many bubbles up to about 1/2 mm in size.

Repeated (two additional) melting of B at 1800°C did not sufficiently improve the seediness and it appears that a higher temperature for refining is needed. The following possibilities

are being explored:

(i) to improve the existing facility of 250 kw, 1 kc induction melting unit to operate under inert atmosphere, using graphite crucible as a susceptor;

(ii) to build a carbon resistor furnace to operate under inert atmosphere;

(iii) to build a gas fired furnace.

An interesting observation made at this stage was the formation of a reddish brown layer on top of glass melt A, presumably of Fe_2O_3 or an iron silicate. This observation was not new. An as-recovered tektite specimen had also developed a similar layer when heated to only about 1300°C in air inside an electric furnace. This phenomena deserves further investigation, since the occurrence of devitrification is an important consideration in diffusion experiments. At the same time, since the as-recovered tektites display no signs of any visual crystallization effects, one may conclude that the cooling of tektites through this temperature range of devitrification must have been rapid enough to avoid crystallization or that the product has weathered away.

DIFFUSION EXPERIMENTS

The following scheme was used for the inter-diffusion experiments.

The specimen preparation was much the same as the one used for K_2O-SrO-SiO_2 glasses. Cylinders of 3/8" diameter were core-drilled from the glasses. They were cut perpendicular to the cylinder axis and the flat faces were ground and polished. Figure 2 shows the diffusion assembly for carrying out diffusion up to about 1400°C.

The couple consists of discs of glass A and either B or C with flat faces in contact and with A placed at the bottom. The housing for the couple was a close fitting graphite sleeve, a graphite plug and two cover plates of graphite. This housing was placed upright in a graphite boat which had a thermocouple inserted in the vicinity of the couple. The assembly was secured with a platinum wire tied around the boat.

Heat treating was carried out in a horizontal tube furnace with an inert (N_2 or Ar) atmosphere.

To start a diffusion experiment, the diffusion assembly was placed inside the tube of the furnace which was at the desired temperature. After an

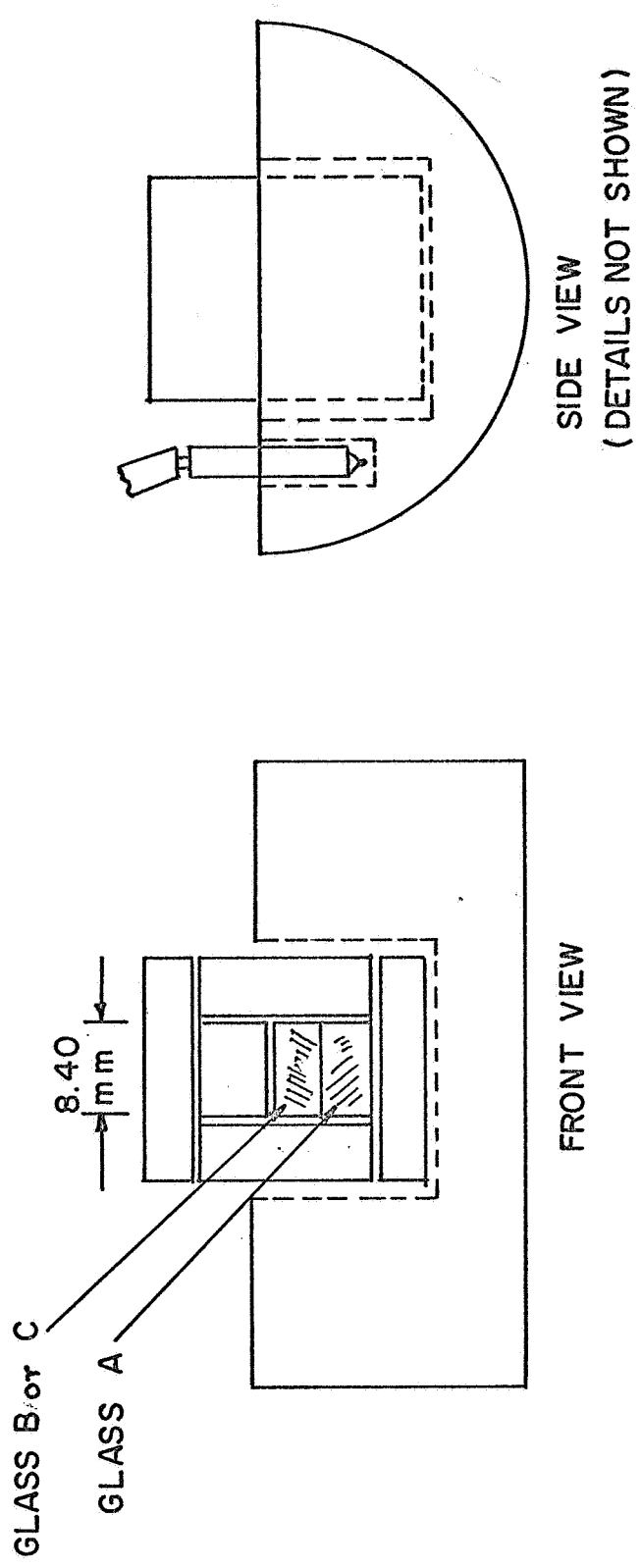


FIG. 2: THE DIFFUSION ASSEMBLY (NOT TO SCALE)

inert atmosphere was assured, the assembly was slid into the hot zone of the tube.

After the elapse of the desired interval of time, the assembly was removed slowly so as not to cause a serious thermal shock to the refractory tube.

THE BLANK

"Blank diffusion runs were of short duration sufficient to cause good sealing of the couple.

In early experiments, it was observed that small bubbles tend to nucleate at the interface of glasses A and C. They grow at ∿1250°C up to about 5 hours after which a gradual dissolution of the bubbles appears to take place.

For this reason, the first 5 hours diffusion anneal was taken as the "blank" diffusion run. The initial conditions of the diffusion couple were then obtained by sawing off a portion parallel to the cylindrical axis of the couple. The remainder of the couple was put back in the diffusion assembly with a graphite piece to compensate for the machined-off portion of the diffusion couple.

Samples in this way were obtained after various diffusion anneals from the same initial set of glass discs until the whole of it was consumed.

ELECTRON PROBE MICROANALYSIS

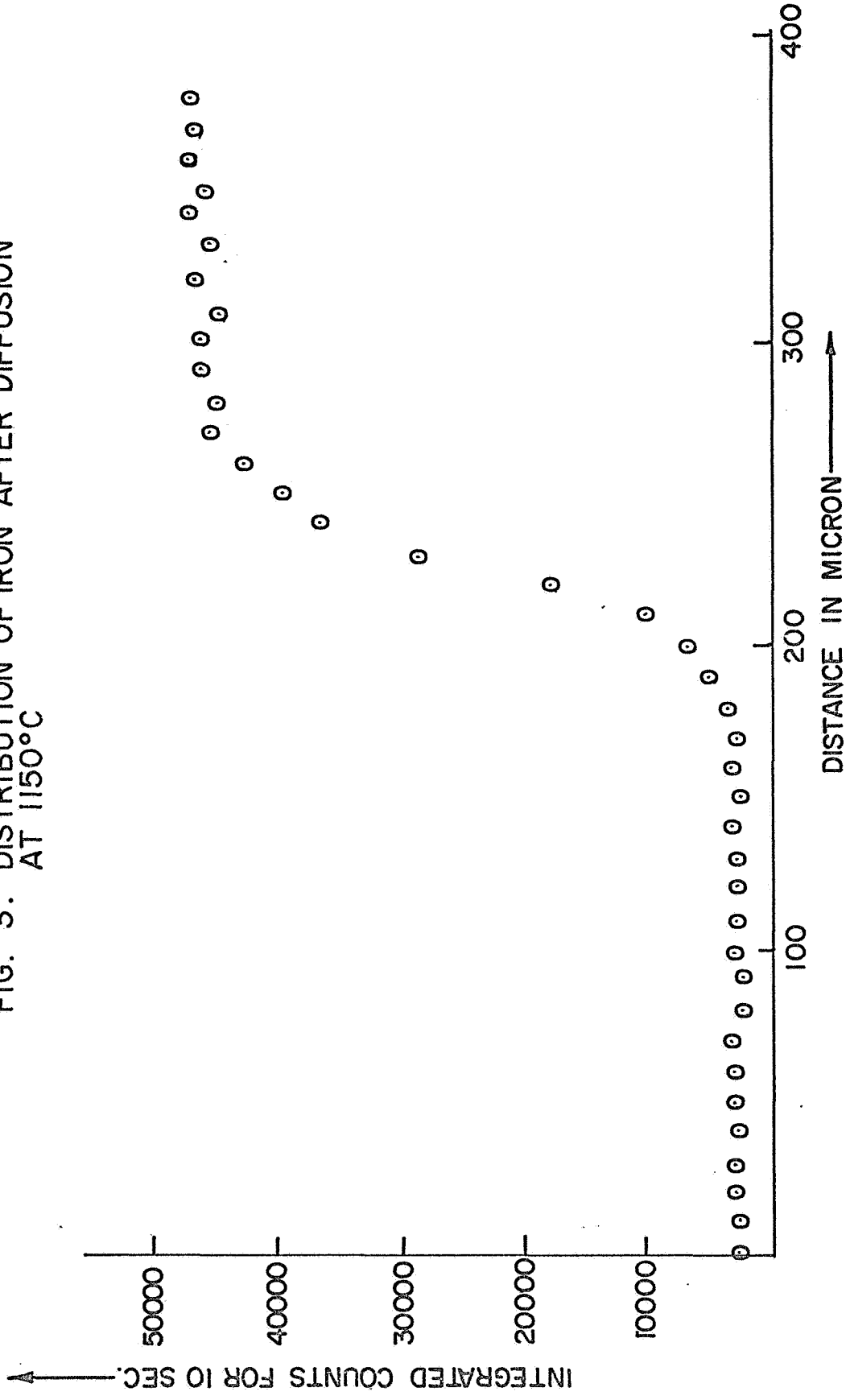
The samples were mounted in a cold mounting medium in a 1" diameter mold with the diffusion direction parallel to the flat face of the mold. After polishing, microhardness indentations were made to mark the interface and a conductive coating of C was vacuum evaporated on the surface of the mount. The specimens were then microanalyzed for the concentration distributions of Fe, Al, Si, Ca and K using an MAC 400 microprobe.

RESULTS

One of the tests to examine the validity of procedures for diffusion experiments is to determine if the diffusion coefficient is independent of time. A diffusion experiment was conducted for this purpose with a couple formed from glass A and glass B at 1150°C. Three samples were obtained from this experiment; corresponding to 6 hours, 26 hours and 100 hours of diffusion time.

The diffusion profiles of iron for these three samples are plotted in Figures 3, 4 and 5 in the form of counts vs distance from an arbitrary point. Figure 6 is a "probability" plot for the three profiles.

FIG. 3: DISTRIBUTION OF IRON AFTER DIFFUSION AT 1150°C



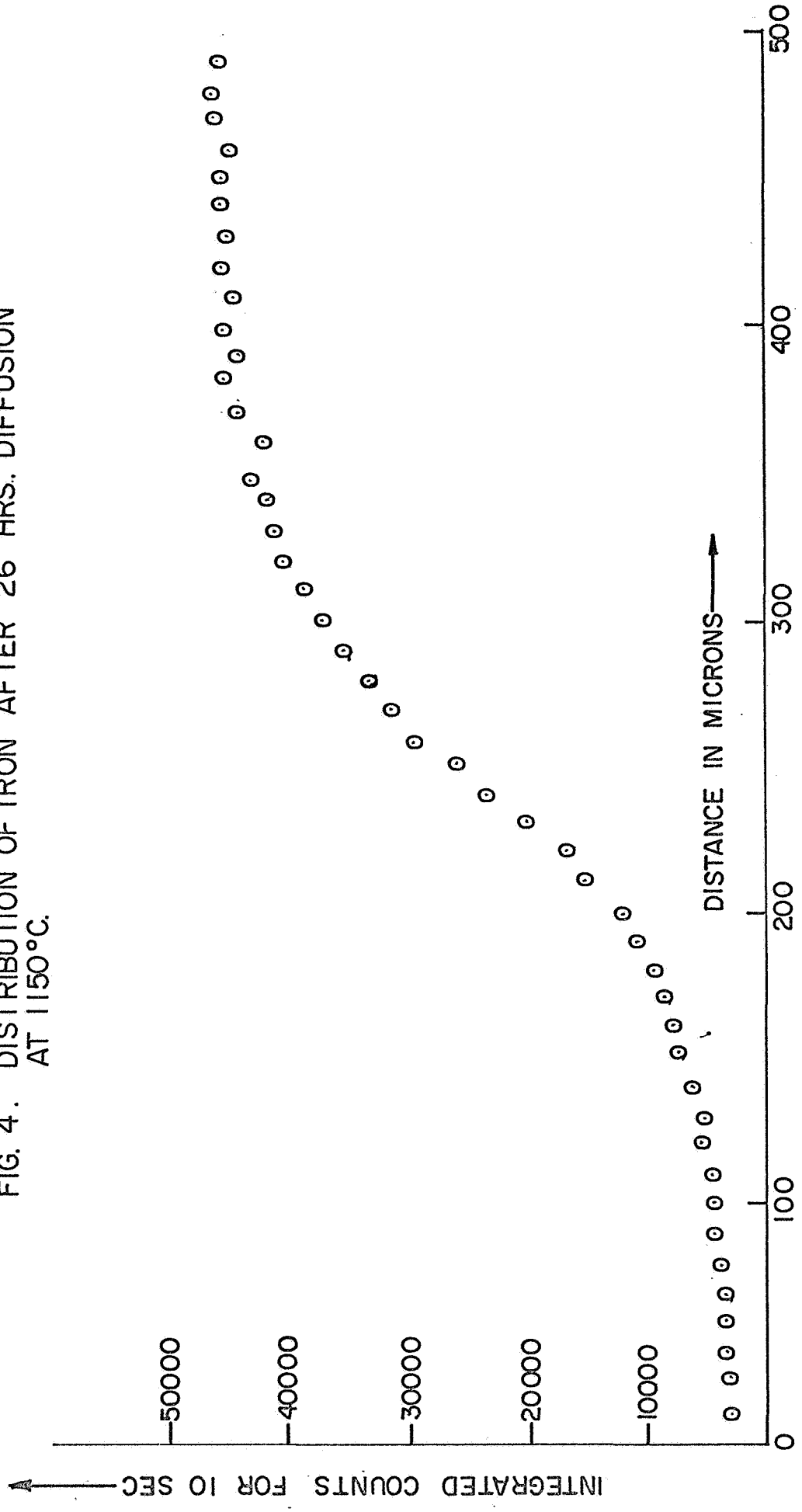


FIG. 4: DISTRIBUTION OF IRON AFTER 26 HRS. DIFFUSION AT 1150°C.

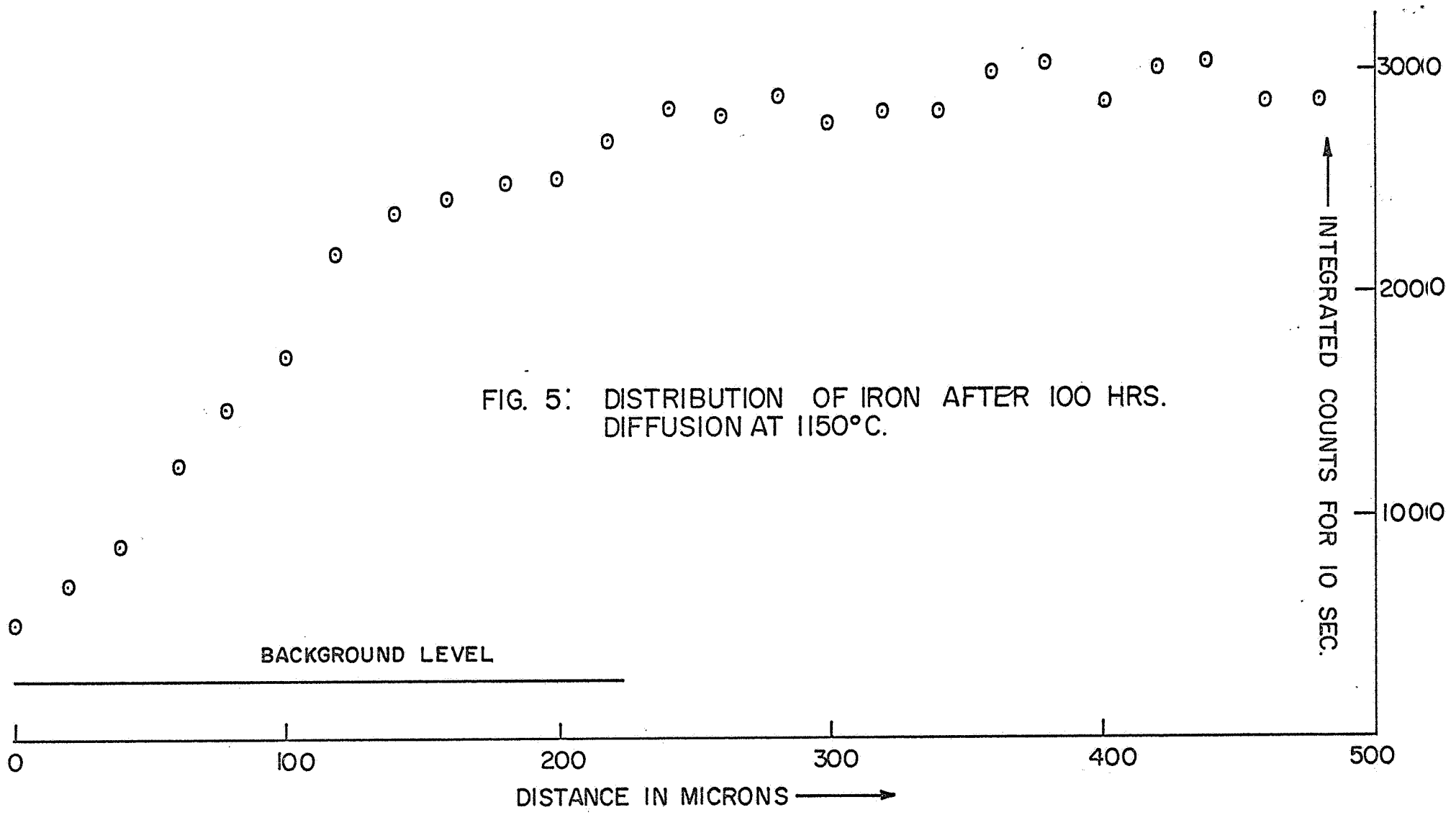
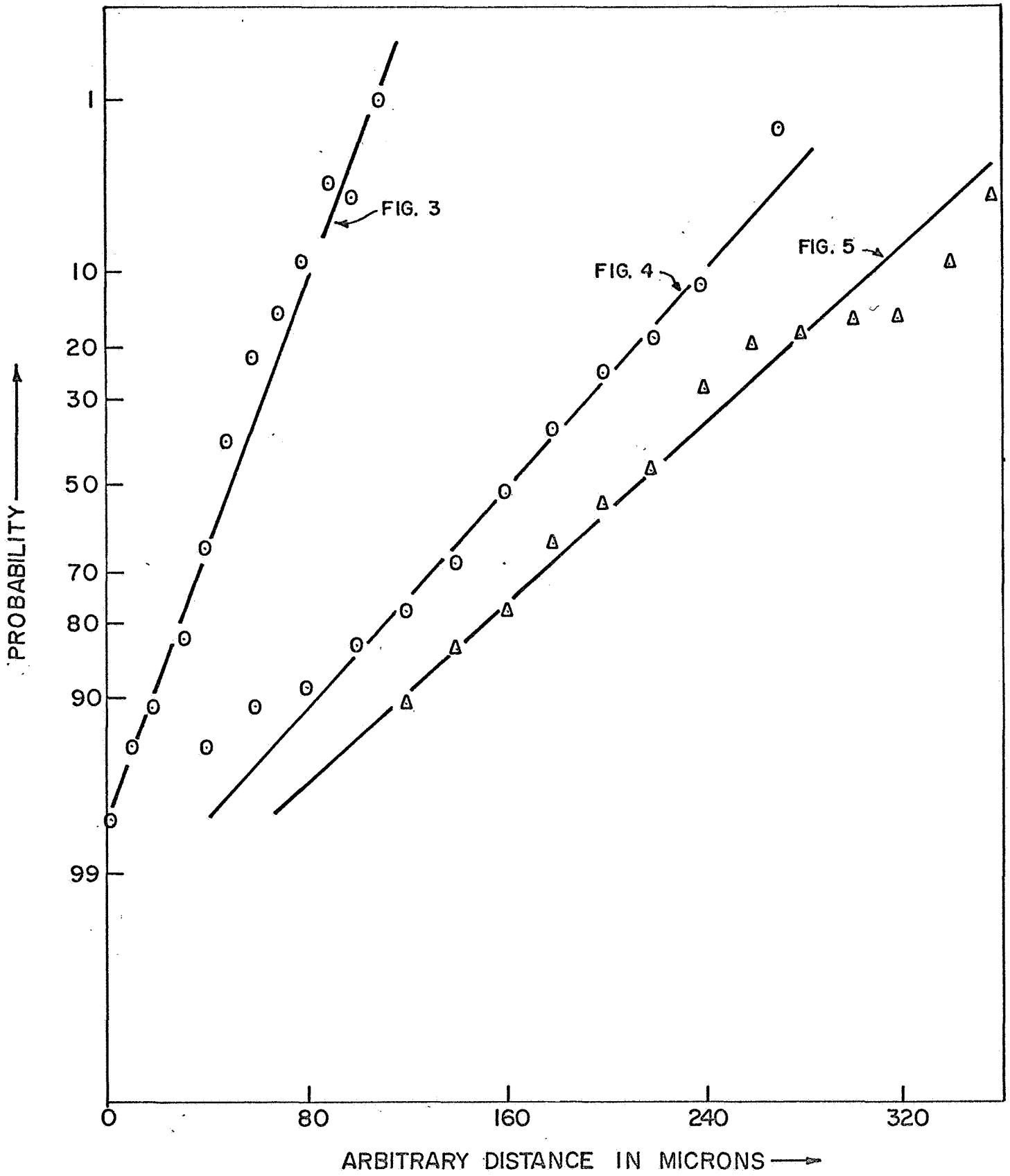


FIG. 5: DISTRIBUTION OF IRON AFTER 100 HRS. DIFFUSION AT 1150°C.

FIG. 6: PROBABILITY PLOT OF IRON DISTRIBUTIONS OF FIG. 3,4 & 5.



An examination of Figure 6 reveals that the concentration distribution of iron could be approximately described by error function equation of the form:

$$C_i = C_o \left[1 + \text{erf } x/2\sqrt{(Dt)}\right] \qquad (1)$$

where C_i = concentration at (x=i)

C_o = concentration at (x=0); the initial concentration

D = effective binary diffusion coefficient which is independent of concentration

The computed values of D_{FeM} from Figure 6 are:

10^{-10} cm^2/sec up to 6 hrs

2.1×10^{-10} cm^2/sec from 6 hrs to 26 hrs

2.4×10^{-11} cm^2/sec from 26 hrs to 100 hrs

While significant deviations from straight lines are not distinguishable on Figure 6, it is clear that our results of D_{FeM} are inconsistent with each other in the sense that they vary by an order of magnitude with time. A probable source of this inconsistency is the interfacial bubbles. The movement of these bubbles during diffusion anneal, can give rise to an apparent diffusivity greater than the true value. If they are immobile, they

might lead to a lower value. Precipitation of the diffusing species could also cause the discrepancy in our results. It should be noted that the microprobe analysis of the 100 hours diffusion run was carried out with a flow proportional counter, whereas a sealed proportional counter was used for the others. The low efficiency of flow proportional counter for the FeK_α wavelength gives rise to a greater scatter as is seen on Fig. 5 and may itself contribute towards the discrepancy between the 100 hour run and the shorter time anneals.

It is obvious that more experiments have to be carried out to ensure the consistency of the results, and these are currently underway.

A diffusion experiment was carried out with glass A and glass C to study the directionality of the effective diffusivity on the composition space. The concentration distribution of iron and calcium in couple A/C after diffusion at 1250°C for 24 hours is shown in Fig. 7. The distributions can still be described by error functions of the form of equation (1), and the effective diffusivity values are calculated to be

$$D'_{FeM} = 6 \times 10^{-10} \text{ cm}^2/\text{sec and}$$
$$D'_{CaM} = 1.7 \times 10^{-9} \text{ cm}^2/\text{sec}$$

Not enough data is available yet to indicate the significance of these results.

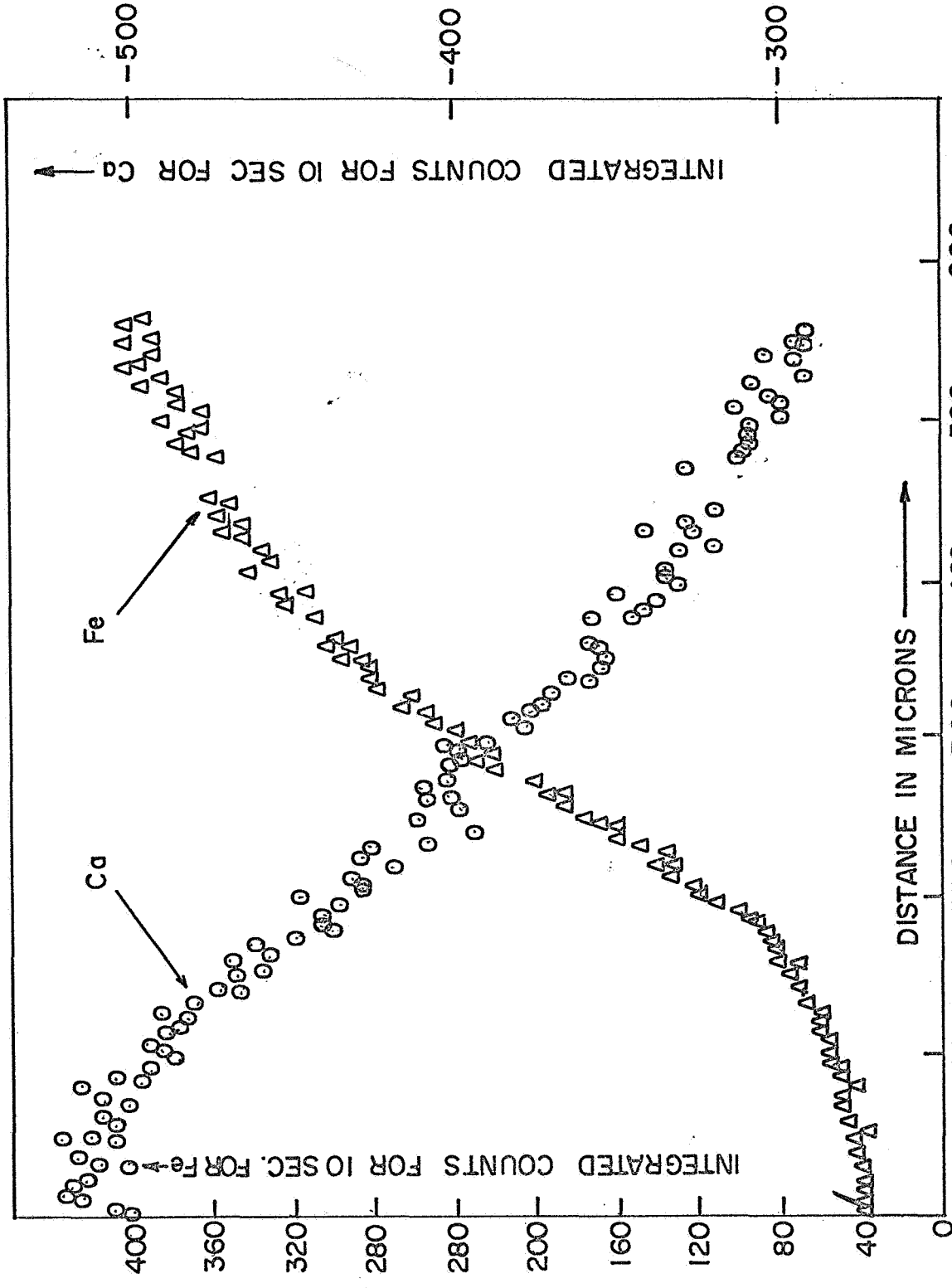


FIG. 7: DISTRIBUTION OF Fe & Ca IN COUPLE A/C AFTER 24 HRS. DIFFUSION AT 1250°C

CONTINUATION OF WORK ON THE K_2O-SrO-SiO_2 SYSTEM

The results reported (1) so far by us have been confined to interdiffusion experiments along only one direction on the composition space of the K_2O-SrO-SiO_2 system. This is indicated on Figure 8 with direction 1. During the past six months data has been obtained along a cross direction, labeled 2 on Figure 8.

The compositions of the glasses used are shown in Table 2.

TABLE 2

Weight Per Cent Composition of the Glasses

	Glass W	Glass Y
K_2O	23.0	20.0
SrO	18.5	17.0
SiO_2	58.5	63.0
Cr_2O_3	--	0.01

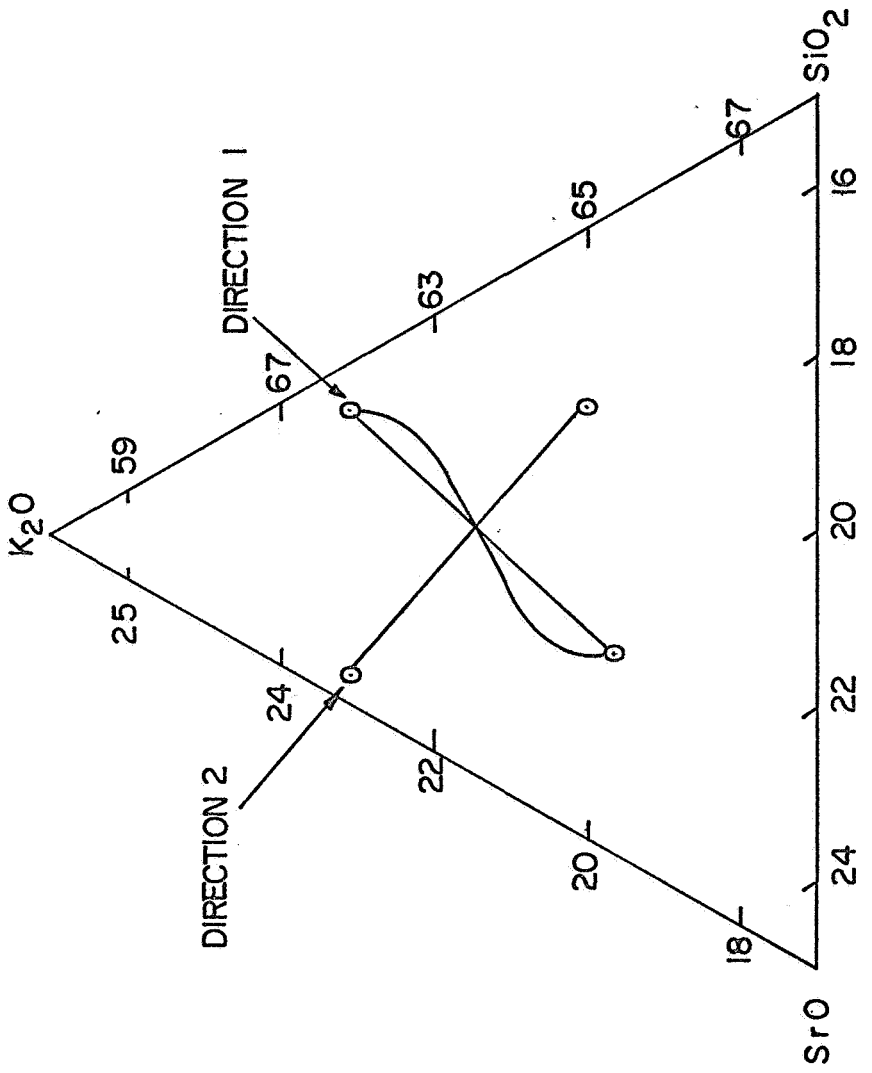

K_2O
SiO_2
SrO
59
25
67
63
65
67
16
18
20
22
24
18
20
22
24
DIRECTION 1
DIRECTION 2

FIG.8

Interdiffusion experiments were carried out at various temperatures in a manner indicated in earlier semi-annual reports.

While most of the specimens are yet to be processed for analysis, the data obtained so far is remarkable.

Figure 9 (a) and (b) shows the concentration distributions of K_2O, SrO and SiO_2 for a sample annealed at 735°C for 7 hours. Figures 10 (a) and (b) are the concentration distributions of K_2O and SrO for a sample at 710°C for 8 hours.

Although the data of Si shows considerable scatter, two features on these figures are striking:

(i) the maximum and the minimum in the distribution of SrO in both the samples;

(ii) the nearness of the K_2O distribution to an error function from which D_{KM} at 735°C (from sample 1) is $\sim 10^{-10}$ cm^2/sec.

Both of these features support the mobility concepts in the effective binary diffusion theory for the multicomponent diffusion. Our interpretation is as follows:

The major concentration gradients in these couples are in the K_2O and the SiO_2 components. Silicon being the least mobile species with a major

FIG.9a: PROFILES OF K_2O AND SiO_2 AFTER DIFFUSION AT 735°C FOR 7 HRS.

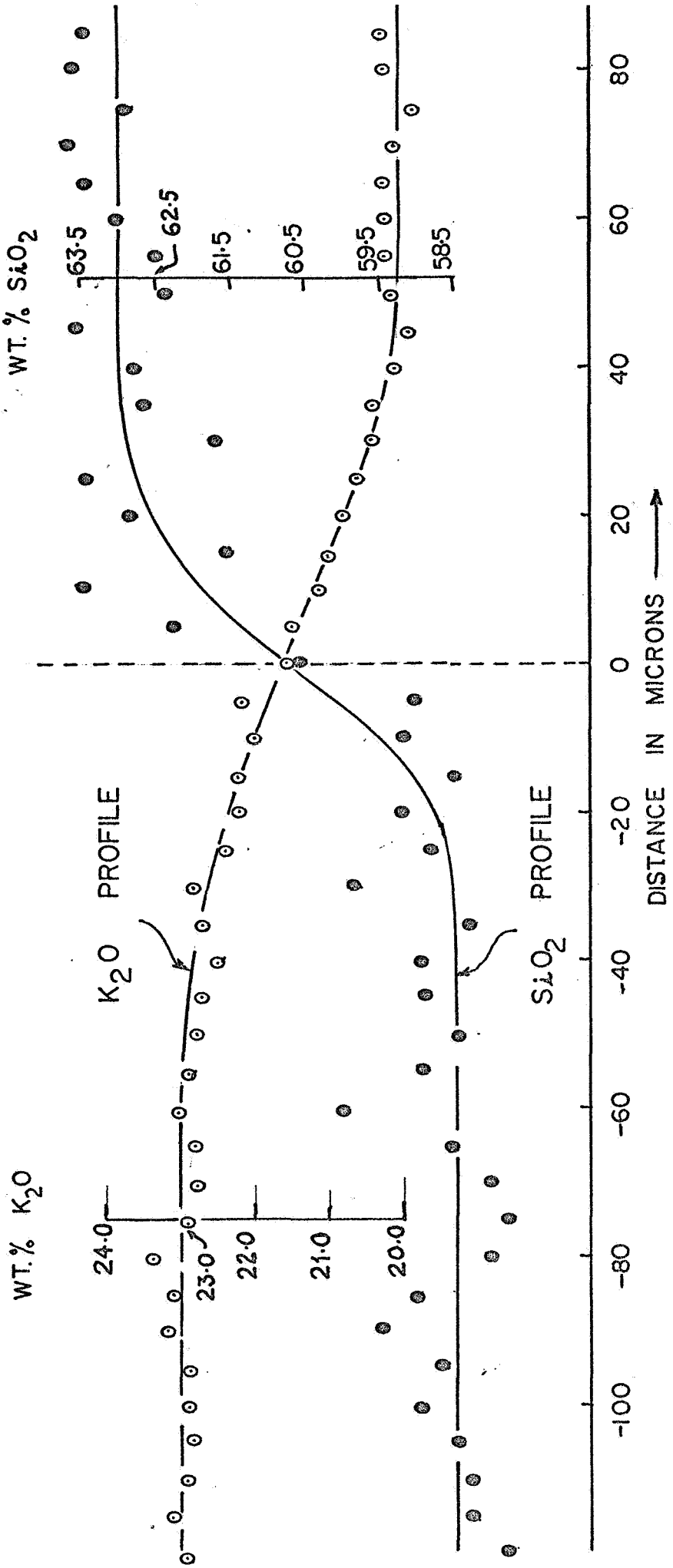
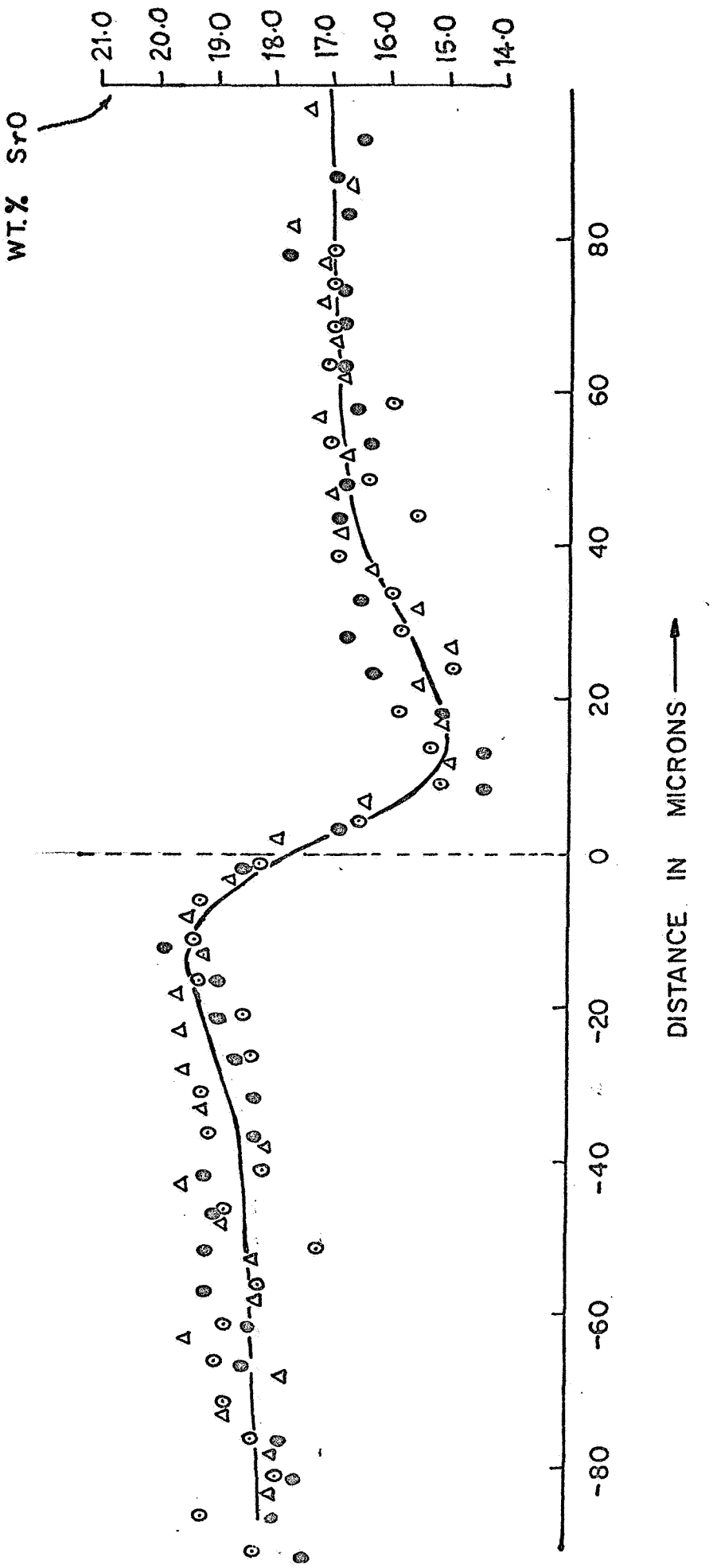


FIG. 9b

DISTRIBUTION OF SrO AFTER DIFFUSION AT 735°C FOR 7 HRS.

(3 PROFILES SUPERIMPOSED)



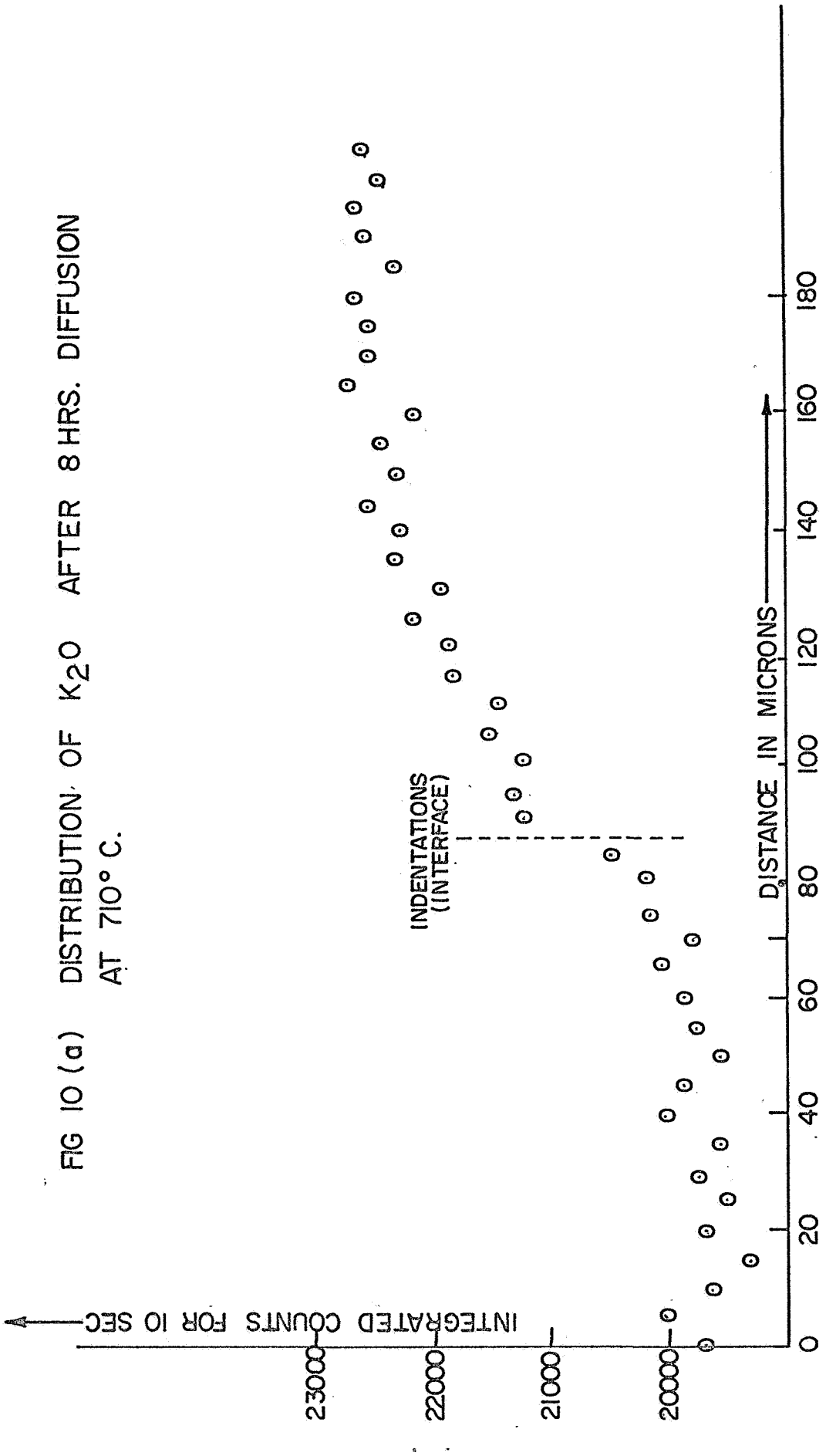


FIG 10 (a) DISTRIBUTION OF K_2O AFTER 8 HRS. DIFFUSION AT 710° C.

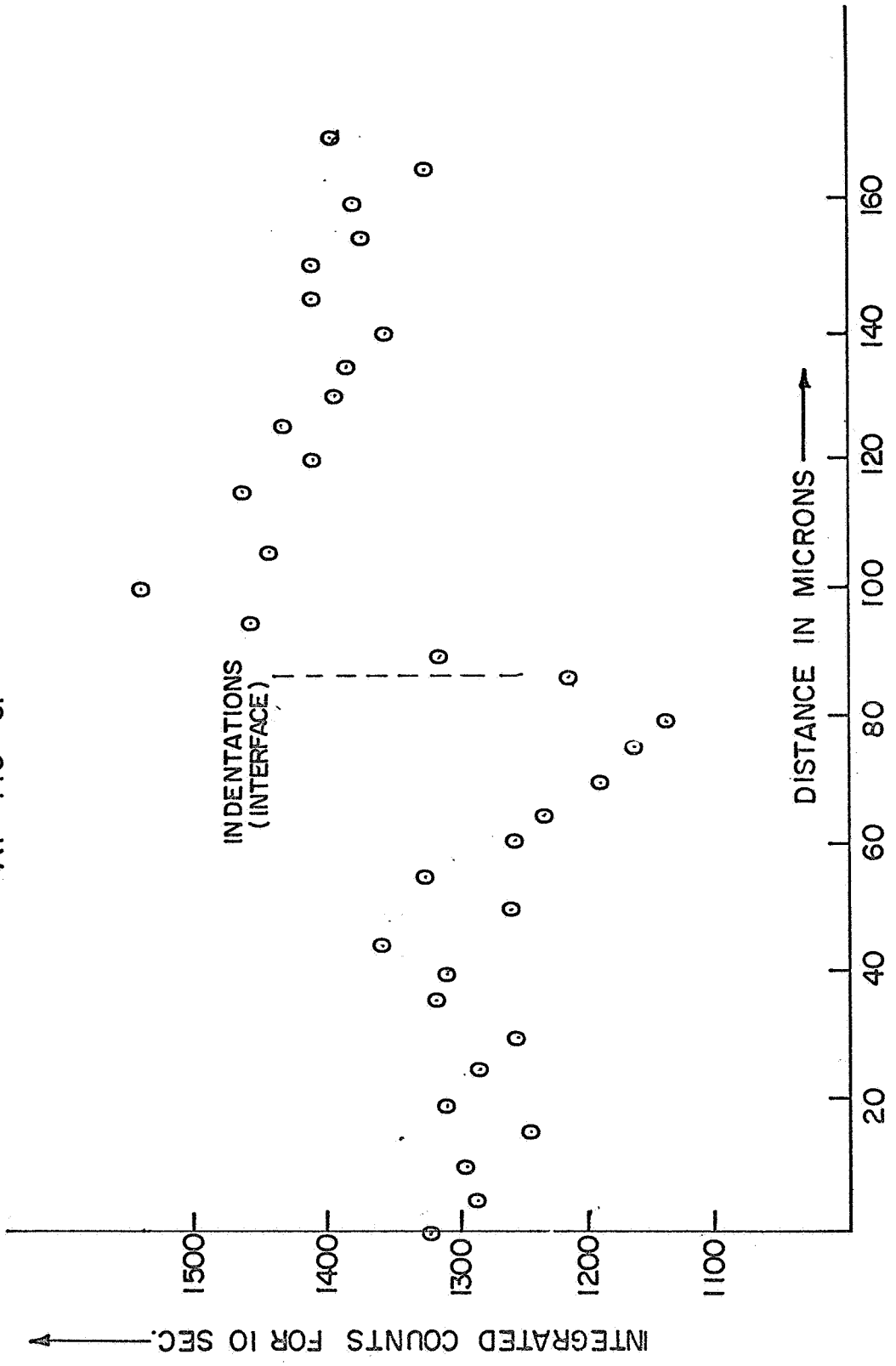


FIG. 10 (b) DISTRIBUTION OF SrO AFTER 8HRS. DIFFUSION AT 710° C.

gradient in the system, controls the kinetics. The high mobility of potassium is retarded by the inability of silicon to move and hence the effective diffusion coefficient of potassium is not the self-diffusion coefficient of potassium (which is about 8×10^{-8} cm^2/sec (2)) but more towards the self-diffusion coefficient of silicon.

The concentration distribution of SrO then occurs due to a mass flow resulting to maintain stoichiometry and charge neutrality in the system. As expected, the value of D_{SrM} is so variable as to be a useless quantity.

SELF DIFFUSION EXPERIMENTS ON TEKTITES

In the foreseeable future, it is expected that some experiments will be carried out on the measurement of the self diffusion coefficient of various species in the tektite system over a range of temperatures. A new concept in preparing a diffusion couple for such experiments is being explored. This involves selective irradiation of a specimen to a neutron flux to yield a steep concentration gradient of the required tracers within the body of the specimen. The biggest advatange in such a procedure would be the omission of interfaces altogether

during the formation of the diffusion couple. Interfaces in a diffusion couple not only act as barriers due to inherent surface flaws but also require a finite time and temperature for their sealing together which denotes the initial t=o condition of the diffusion couple. It is believed that with the use of such a technique, diffusion coefficients whose values are low could be determined with a precision better than the ones from conventional experiments.

PRODUCTION OF ^{32}Si

Part of the attention this six months has been focused on producing ^{32}Si isotope by triton irradiation (half life ~750 years β^-_{max} = 100 kev). Owing to its long half life, the isotope would enable more precise measurements on the diffusion characteristics of Si to be made than what have been possible so far.

One of the methods to produce ^{32}Si is the ^{30}Si (t,p) ^{32}Si reaction. In the past, this reaction has been carried out by irradiating an Li_2Si alloy with a thermal neutron flux in a reactor.[3] ^6_3Li has a high cross section (950 barns) for thermal neutrons yielding tritons through the reaction

$$^6_3Li + ^1_0n \rightarrow ^3_1H + ^4_2He$$

The liberated tritons then react with the ^{30}Si to form ^{32}Si. An estimate of the effective cross section in this process is about 0.5 mb. With this cross section, the activity level of ^{32}Si produced would not be high enough to obtain statistically meaningful diffusion measurements with the counting facilities at Case.

Following a suggestion from Dr. James Blue, of NASA Lewis Research Center, we attempted to produce ^{32}Si

by a direct bombardment of 10 mev tritons (beam current 3μa for 8 hours) upon a 95.2% enriched powdered ^{30}Si metal target inside the Los Alamos triton accelerator.

An assay was made as to the quantities of ^{32}Si in the material after a lapse of about 2 1/2 months. This was done by:

(i) obtaining an absorption curve of the radiation emitted;

(ii) following the decay by counting the intensity under standard geometry.

Both methods have indicated that at an energy level of 10 mev, the (t,n) reaction is much more favorable than the (t,p) reaction. Due to the overwhelming activity of ^{32}P, the detection of ^{32}Si in the reaction products is only possible after a lapse of a considerable length of time, perhaps as much as five more months.

It thus appears that there is a need for determining the level of favored energies for the (t,p) reaction. Experiments in this direction are under investigation.