this tail-off results from the last two processes listed above. When the sample material is finely powdered and compressed into a pellet, it is reasonable to expect nucleation from many centers (such as corners and edges of grains, and defect sites). It is very likely that such nucleation is similar to that observed in calcite annealing experiments such as those carried out by *Griggs et al.* [1960a, p. 31]. These authors observed from 5 to 10 new crystal nuclei growing from an individual calcite host grain. Furthermore, a compressed pellet will retain strain energy (anelastic) which, because of its distribution on edges and corners of a grain, can aid in surmounting the energy barrier for the transformation. Stored strain energy is known to lower the annealing temperature of cold-worked aggregates [*Buerger and Washken*, 1947; *Griggs et al.*, 1960a] and is thought to have increased the transition rate enstatite → clino-enstatite [*Griggs et al.*, 1960b, p. 62].

Because the first parts of the grains to transform are the edges and corners, it follows that the transition rate will decrease as these regions are eliminated from the reactant phase. The tail-off observed is thus the combined effect of a decrease in available sites for nucleation and a decrease in anelastic strain energy. It is distinctly possible that there are other processes that may so modify the rate of transformation, but, if one considers only the two discussed above, the transformation curves can be more appropriately described by the relation

$$dx/dt = K_0 + K_n(x_0 - x)^q + K_s(x_0 - x)^r \qquad (3)$$

where the rate constant K_0 describes pure growth of the boundary separating reactant from product phase, and the last two terms, equivalent in form to the right-hand member of (1), describe the nucleation rate and the rate of dissipation of strain energy during the transformation. Little can be done with (3) until more is known about the order of rates of nucleation in solid-state processes such as annealing and polymorphic transformation. However, on the basis of the present hypothesis it would be expected that the value of p in (1), for rates in which the sample is a uniformly heated and annealed loose powder, would be very small. This effect would be due to the lack of strain energy that otherwise would be introduced into

the sample if a pellet were to be made. The linear rates observed by Brown et al. for loose powders spread on a heating block appears to offer some qualitative experimental verification of this hypothesis.

Effect of temperature and pressure and geologic implications. Table 1 and Figure 5 demonstrate the marked effect of temperature on the amount of tail-off (value of p) and magnitude of the rate constant. If the mechanisms of transformation previously described are operative, these mechanisms change with lowering temperature and with increasing pressure. However, a constant activation energy is indicated by the linear relationship of $1/T°K$ versus $-\log K$, and $1/T°K$ versus log time for 40% transformation. The activation energy for the aragonite → calcite transformation at 1 bar is calculated from the Arrhenius equation to be 106 kcal/mole. *Chaudron* [1952] obtained a variety of values for the activation energy for this transformation, depending on the sample used. For a natural aragonite he obtained 80 kcal/mole, whereas for synthetically precipitated aragonite he obtained half this value.

There is also an obvious retarding effect of pressure on the aragonite → calcite transformation. Consider, for example, the relative transformation rates at 1 bar and at 8 ± 1 kb for a temperature of 400°C. To calculate the transformation times we integrate (1) to obtain

$$t = \frac{1}{(p - 1)K} [(x_0 - x)^{1-p} - (x_0)^{1-p}] \qquad (4)$$

in which the constant of integration was determined from the initial conditions $x = x_0$ at $t = 0$. Taking values of p and k from Table 1 we obtain for 99% conversion $t = 3.18 \times 10^4$ min at 400°C and 1 bar and $t = 2.38 \times 10^{13}$ min at 400°C and 8 ± 1 kb. This results in a pressure effect at this temperature of 10^9 for *nearly complete conversion*. Note, however, from Figures 2B and 3A that when $x < 50$ the pressure effect is less than 20:1. This phenomenon is not unexpected when one considers the different degrees of tail-off (i.e., differing magnitudes of p) for each transformation curve.

Even though such conclusions as that presented above are made less reliable by the existing pressure uncertainty, the results are sufficiently quantitative to allow construction of a series of isochronous (equal time) lines in a portion of
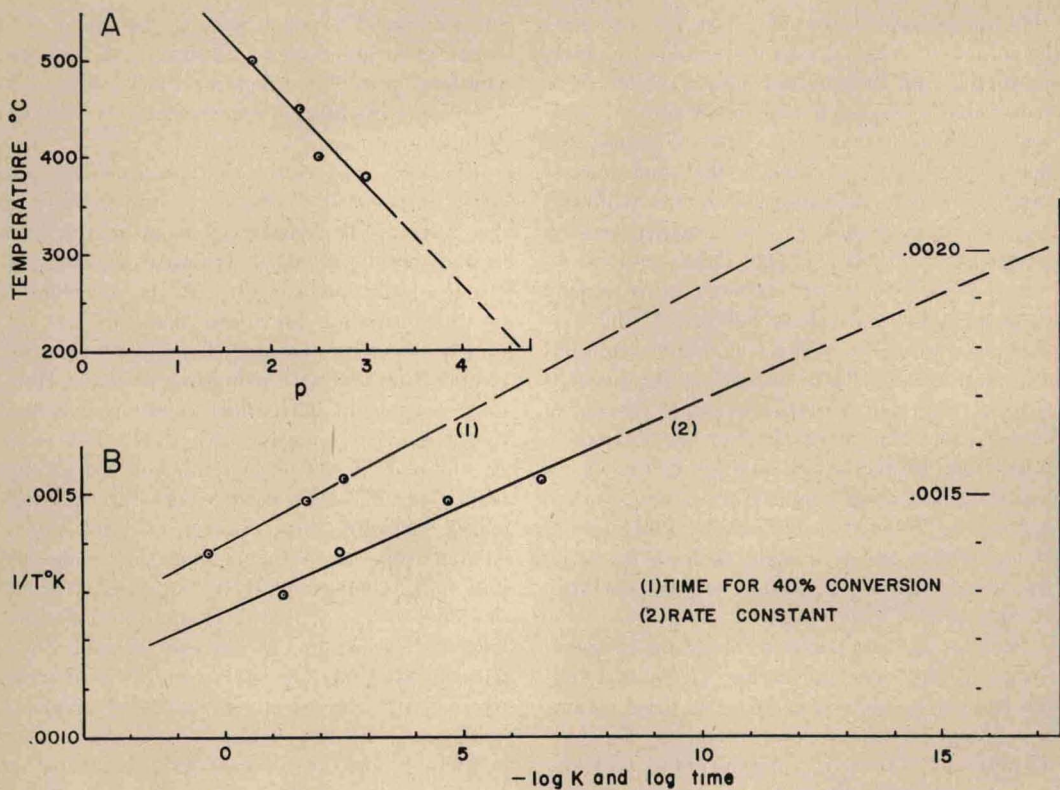
Fig. 5. A; plot of the exponent p of equation 1 versus $T°C$ for Kamsdorf aragonite calcite at 1 bar (beryllium pressure vessel). B; plot of $-\log K$ and log time for 40% conversion versus $1/T°K$ for Kamsdorf aragonite → calcite at 1 bar (beryllium pressure vessel).

the calcite stability field (Figure 6). The curves were constructed from the data of Table 1 as well as calculated transformation times using (1); they represent the time in minutes (5.3 × 10^5 min/year) required to obtain 99% conversion of aragonite to calcite. The curves approach the phase boundary asymptotically, as is compatible with conditions of equilibrium. Of interest is the fact that in any retrograde geologic situation aragonite would undergo changing conditions of pressure and temperature along a near-linear geothermal gradient and would cross several isochrons twice, first very close to the equilibrium boundary and then again at lower temperatures and pressures. The bulk of the transformation would still take place along the higher reaches of the geothermal gradient, however, where the pressures are only a few hundred bars below the phase boundary.

The results of this study lead to a value for the paleogeothermal gradient in the Franciscan metamorphic rocks of 11 to 12 deg/km, which is somewhat higher than the 10 deg/km proposed by Brown et al. [1962]. Such calculations are made by assuming that the bulk of the conversion takes place along a restricted high-temperature portion of the gradient curve that lies far enough below the intersection of gradient curve and calcite-aragonite equilibrium boundary to permit one to estimate the magnitude of the pressure effect on the rates. The pressure effect used here was 10^9. Our calculations are based on the Kamsdorf aragonite transformation times, which are roughly one-fourth as large for complete conversion as the metamorphic material (see Figure 4C). This difference will not affect our conclusions appreciably.[3] The major

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[3] Because of the smaller transformation rates of the metamorphic aragonite, the value allowable for the paleogeothermal gradient would be slightly greater than that for the Kamsdorf aragonite.