

Kinetics of the Calcite \rightleftharpoons Aragonite Transformation¹

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Abstract. A beryllium pressure vessel mounted in an X-ray diffractometer has been used to study the rates of the transformation calcite \rightleftharpoons aragonite at temperatures to 500°C and pressures to 15 kb. The rates of transformation are shown to be both temperature and pressure dependent. It is proposed that the tail-off shown by all rate curves presented here results from a decrease in nucleation and loss of stored strain energy in the sample as the transformation progresses. In the vicinity of 400°C the rate of the calcite \rightarrow aragonite transformation at 15 ± 1 kb is similar to the reverse transformation at 1 bar. A decreasing-temperature extrapolation of the rate constant for the aragonite \rightarrow calcite transformation shows that this transformation at room temperature progresses at a negligible rate. The activation energy for this transformation at 1 bar is 106 kcal/mole. The use of the experimental rate data as well as calculated transformation times obtained from an empirical relationship describing the transformation has permitted the construction of curves of time for 99% transformation of aragonite \rightarrow calcite in the portion of the calcite stability field lying below 500°C.

INTRODUCTION

Some understanding of the structural properties of solids can be gained through a study of the speeds by which one polymorphic form will transform to another. Both the transformation velocities and the shapes of the rate curves can give information as to the type of transformation involved (i.e., whether reconstructive, displacive, etc.) and whether certain physical characteristics of the sample environment are speeding up, or retarding, the transformation. A classic example of this type of study is that carried out by *Bridgman* [1915] in which various solid-solid transformation rates were studied at constant volume.

A detailed study of the transformation rates for calcite \rightleftharpoons aragonite is presented here. Previous work includes that of *Chaudron* [1952], where the transformation at 1 atmosphere was followed continuously by a dilatometric method, and that of *Brown et al.* [1962], in which the rate curves were constructed from data of separate heating experiments also at 1 atmosphere. In both the above only the aragonite \rightarrow calcite

transformation was studied. Using ultrasonic pulse interferometry, *Ahrens and Katz* [1963] reported a minimum in longitudinal elastic wave velocity of 4.8 km/sec at room temperature and 8 kb in Solenhofen and Manlius limestones. They suggest that the minimum is due to a reversible transformation of calcite to aragonite. T. J. Ahrens (personal communication) proposes that the otherwise sluggish transformation was induced by shear stresses present in their apparatus.

EXPERIMENTAL METHOD

The experimental apparatus consists of a supported beryllium cylinder mounted on a X-ray diffractometer. Details of the apparatus and procedure have been described previously [*Davis and Adams*, 1964]. Several experiments were also carried out at 1 atmosphere using a heating stage designed by the M.R.C. Manufacturing Company.

The aragonite starting material was single-crystal aragonite from Kamsdorf bei Saalfeld, Saale (Germany), and a Franciscan metamorphic aragonite from Pacheco Pass, California. Only the former was used in the supported beryllium cylinder, but a comparison of the Kamsdorf and Pacheco Pass rates can be made from the experiments on the high-temperature stage. A finely precipitated synthetic CaCO_3 was used for the calcite starting material.

¹ Publication 387 of the Institute of Geophysics and Planetary Physics, University of California, Los Angeles.

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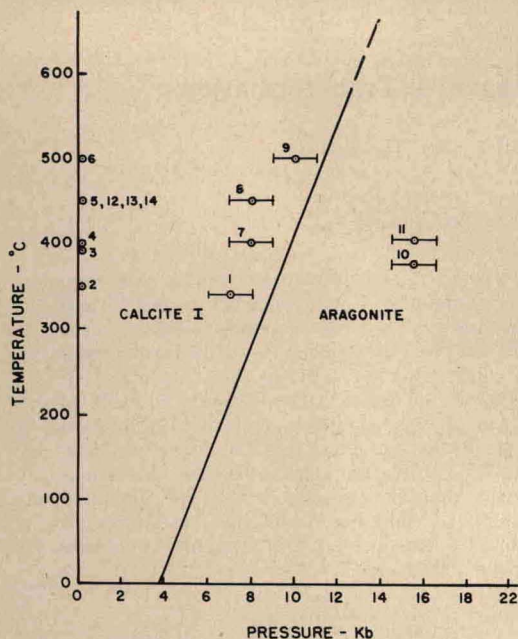


Fig. 1. Partial phase diagram of CaCO_3 showing known stability fields of calcite and aragonite and P - T coordinates of the experiments. The pressure uncertainty is indicated by the short horizontal lines.

The experiments are of four types:

(1) Aragonite \rightarrow calcite at temperatures from 300°C to 500°C, at atmospheric pressure, using the beryllium pressure vessel. Aragonite starting material was kept under pressure high enough to remain in the stability field of aragonite while the temperature was raised to the desired value. The pressure was then dropped to atmospheric and the rate recorded.

(2) Aragonite \rightarrow calcite at temperatures from 340°C to 500°C, at pressures near that of the equilibrium boundary (Figure 1), using the beryllium pressure vessel. As in (1) the aragonite starting material was kept in its equilibrium field until the desired temperature was reached, whereupon the pressure was dropped to just below that of the phase boundary into the calcite stability field.

(3) Calcite \rightarrow aragonite at 375°C and 405°C and at pressures considerably above the phase boundary. To obtain the pressure desired it was necessary to apply the pressure to the calcite starting material first and then to raise the temperature. Up to the two temperatures involved

the transformation rates were not great enough to convert more than 1 or 2% of calcite to aragonite before the temperature had reached the desired value. Any significant amount of transformation would, of course, be noted by the growth of aragonite peaks while the temperature was being elevated.

(4) Aragonite \rightarrow calcite at 450°C and at atmospheric pressure, using the M.R.C. heating stage. Here the temperature for the experiment was attained in about 5 seconds. Initial material was both Kamsdorf and Franciscan aragonite.

All rates were recorded by oscillating the goniometer about known peak localities for the product phase. The proportion of aragonite in the sample was determined from the ratio.

$$R = \frac{I_{104}^c}{I_{012}^a + I_{021}^a + I_{111}^a}$$

where I is the integrated intensity for the hkl reflection indicated. The superscripts a and c refer to aragonite and calcite, respectively. R was plotted against measured volume proportion of aragonite in calcite-aragonite aggregates. The several aragonite peaks were included in the ratio to help eliminate intensity anomalies due to preferred orientation on one or both of the two good aragonite cleavages. Calcite always becomes preferentially oriented on 104.

Figure 1 is a partial phase diagram of CaCO_3 [MacDonald, 1956; Jamieson, 1953; Clark, 1957] showing the P - T coordinates of the experiments. Pressures were determined from prior calibration of the vessel [Davis, 1964, p. 24]. The temperature uncertainty in the beryllium vessel is $\pm 2^\circ$, but the uncertainty for the M.R.C. high-temperature stage is probably between 10 and 20°.

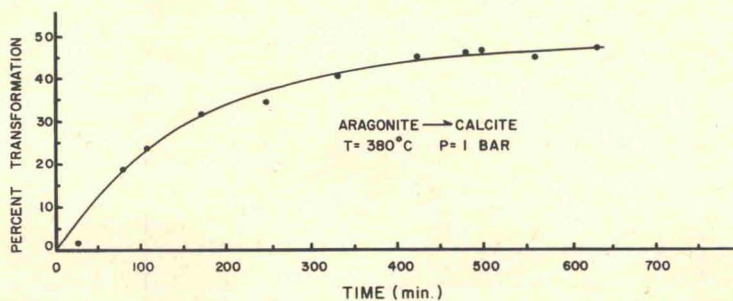
RESULTS

Figures 2 to 4 present the observed rate curves in terms of per cent transformation versus time. Figure 4, *C* and *D*, contains three of the rate curves determined at atmospheric pressure using the M.R.C. high-temperature stage.

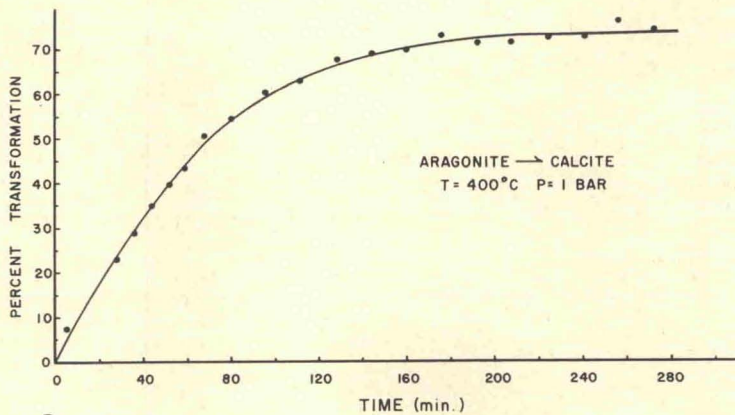
All rate curves, with the exception of that in Figure 4*D*, can be fitted to a general rate expression of the form

$$dx/dt = K(x_0 - x)^p \quad (1)$$

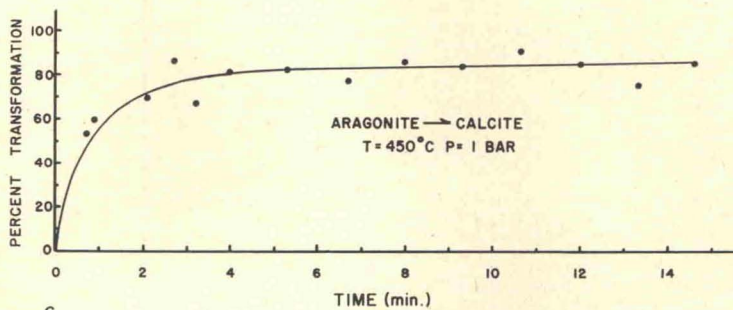
where x_0 and x are, respectively, the initial quan-



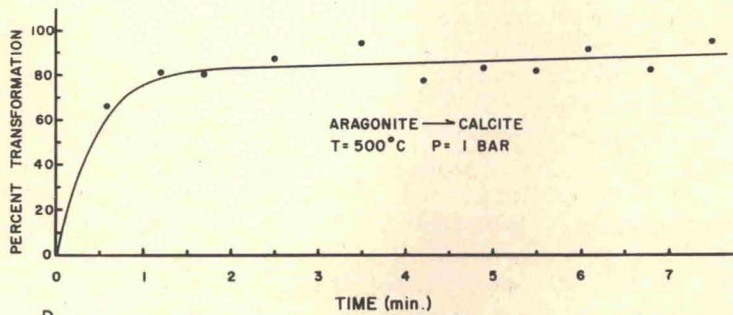
A



B



C



D

Fig. 2. Observed rates of transformation for Kamsdorf aragonite \rightarrow calcite at 1 bar in the beryllium pressure vessel: A, at 380°C; B, 400°C; C, at 450°C; and D, at 500°C.

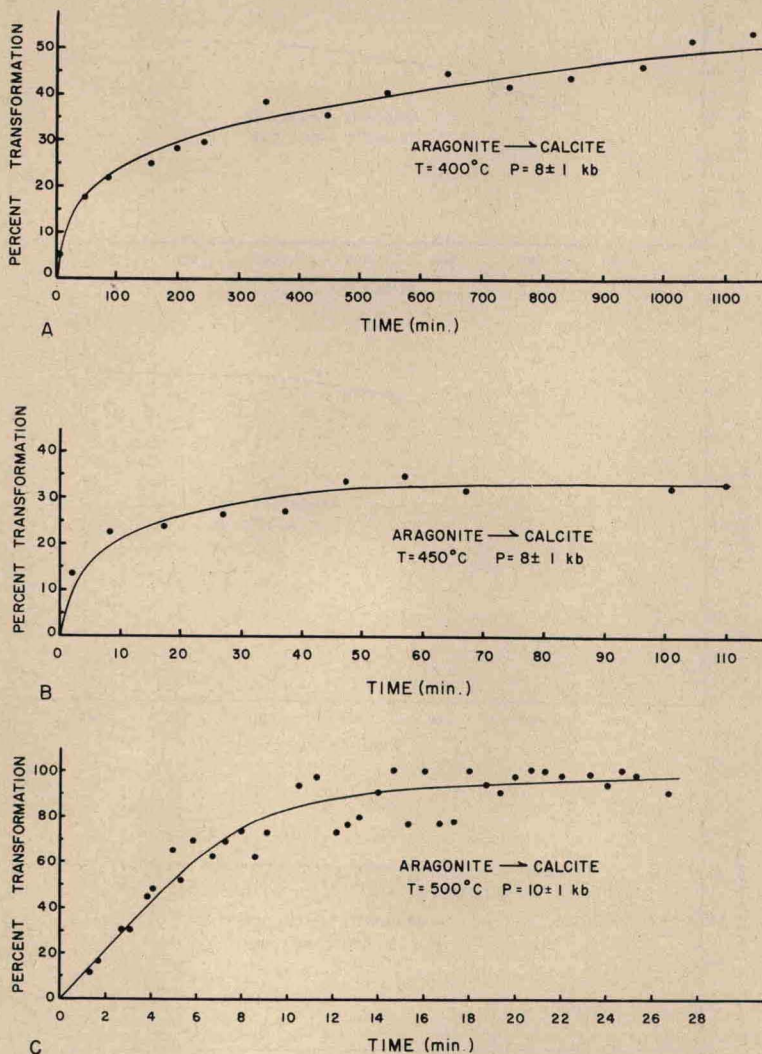


Fig. 3. Observed rates of transformation for Kamsdorf aragonite \rightarrow calcite: A, at 400°C and 8 \pm 1 kb; B, at 450°C and 8 \pm 1 kb; and C at 500°C and 10 \pm 1 kb. Beryllium pressure vessel.

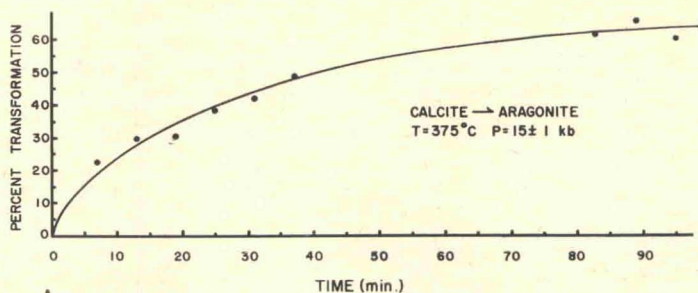
tity and the quantity at time t of reactant phase, K is a rate constant, and p is a number (positive, but not necessarily integral) analogous to the 'order' of chemical reactions. The units of K are (per cent) $^{1-p}$ /min when x is given as per cent of the initial quantity of reactant phase x_0 . The rate curve of Figure 4D was fitted approximately to equation 1 by using the dashed line.

The method for finding the values of p and K for each rate curve, where p is thought *not* to be integral, involves finding the slopes dx/dt at various values of x along the rate curve and then adjusting the value of p in $(x_0 - x)^p$ so that

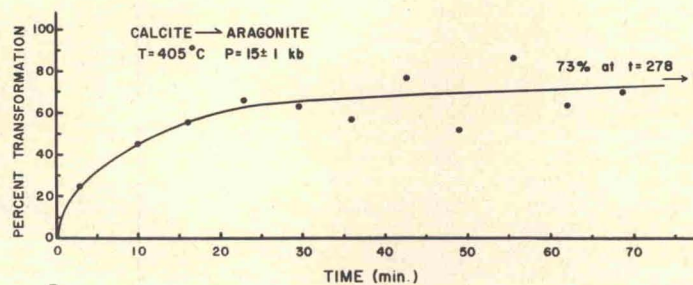
$$\begin{aligned} \frac{m_1}{(x_0 - x_1)^p} &= -\frac{m_2}{(x_0 - x_2)^p} = \frac{m_3}{(x_0 - x_3)^p} = \dots \\ &= \frac{m_i}{(x_0 - x_i)^p} = K \end{aligned} \quad (2)$$

where $m = dx/dt$. The rate curve itself was fitted by eye to the experimental points.

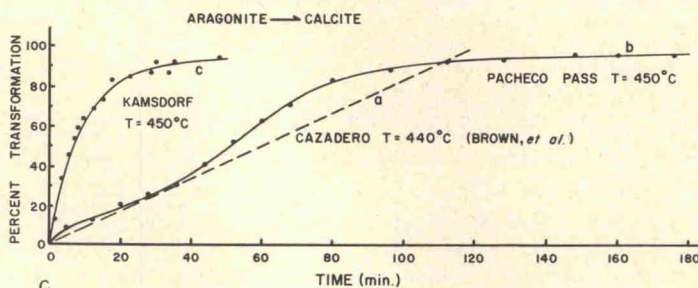
The rate data of this study are summarized in Table 1. The closeness of fit of this data to (1) is indicated by the standard deviation divided by the mean value (fract. dev.) for the determination of K for five such terms as given in (2).



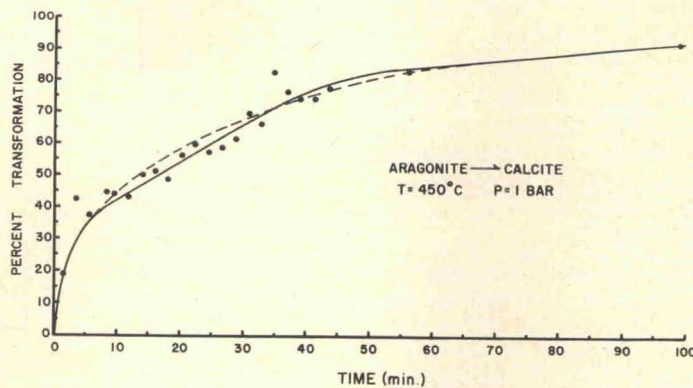
A



B



C



D

Fig. 4. Observed rates of transformation for calcite \rightleftharpoons aragonite: A, Kamsdorf calcite \rightarrow aragonite at 375°C and 15 \pm 1 kb in the beryllium pressure vessel; B, Kamsdorf calcite \rightarrow aragonite at 405°C and 15 \pm 1 kb in the beryllium pressure vessel; C, Cazadero metamorphic aragonite \rightarrow calcite at 440°C and 1 bar (curve a) as observed by

Brown *et al.* [1962], Pacheco Pass aragonite \rightarrow calcite at 450°C and 1 bar in the M.R.C. heating stage (curve b, exp. 12), Kamsdorf aragonite \rightarrow calcite at 450°C and 1 bar in the M.R.C. heating stage (curve c, exp. 13); D, Kamsdorf aragonite (with 10% quartz) \rightarrow calcite at 450°C and 1 bar in the M.R.C. heating stage (exp. 14).

TABLE 1. Rate Data Obtained from Fourteen Experiments on the Calcite \rightleftharpoons Aragonite Transformation at High Temperatures and Pressures

Experiment			Temp., °C	Press., kb	X_{\max} , %	t_{\max} , min	p	K (%) ^{1-p} /min	Fract. Dev.	Tech.*
No.	Class	Rate								
1	2	A-C	340	7.0	0	1560				B
2	1	A-C	350	0.001	9	355	3.2†	1.2×10^{-8}		B
3	1	A-C	380	0.001	52	632	3.0	2.3×10^{-7}	0.47	B
4	1	A-C	400	0.001	74	284	2.5	2.1×10^{-5}	0.23	B
5	1	A-C	450	0.001	86	18	2.3	3.8×10^{-3}	0.18	B
6	1	A-C	500	0.001	96	9	1.8	5.8×10^{-2}	0.26	B
7	2	A-C	400	8 ± 1	53	1143	7.0	7.0×10^{-15}	0.11	B
8	2	A-C	450	8 ± 1	34	112	10.0	8.1×10^{-20}	0.19	B
9	2	A-C	500	10 ± 1	92	25	1.5	3.7×10^{-2}	0.21	B
10	3	C-A	375	15 ± 1	63	95	3.0	3.8×10^{-6}	0.20	B
11	3	C-A	405	15 ± 1	73	678	3.0	1.2×10^{-5}	0.17	B
12	4	A-C	450	0.001	97	48	1.2	4.3×10^{-2}	0.12	S
13‡	4	A-C	450	0.001	95	200	1.8	4.2×10^{-3}	0.23	S
14§	4	A-C	450	0.001	92	99	1.5	5.4×10^{-3}	0.41	S

* B = beryllium vessel; S = M. R. C. high temperature stage.

† p extrapolated (see Figure 5A).

‡ Pacheco Pass aragonite.

§ Kamsdorf aragonite with 10% quartz.

Figure 4, A and B, shows two transformation curves for calcite \rightarrow aragonite at 15 ± 1 kb and 375°C and 405°C , respectively. For the forward reaction (calcite \rightarrow aragonite) these were the only useful records obtained under these conditions. It is possible that this transformation involves the temporary appearance of CaCO_3 -II inasmuch as this phase is thought to be metastable with respect to aragonite in this P - T region [Jamieson, 1957]. Most calcite \rightarrow aragonite experiments had to be discarded because the beryllium pellet above the sample commenced to extrude rapidly above 400°C , and in only a few minutes at this temperature and 15 kb the X-ray beam was entirely cut off from the sample. The small rate constant of experiment 8 is anomalous in comparison with experiments 7 and 9 and can best be explained by the actual pressure being closer to the equilibrium boundary than that estimated from the calibration curves.

DISCUSSION

Mechanisms of transformation. One of the most obvious features of the rate curves is the considerable tail-off. Some curves can be fitted to (1) only with very large values of p (experiments 7 and 8, Table 1). It should be emphasized here that for a solid-state reaction such as this p does not have the same physical sig-

nificance as does the familiar 'order' of a chemical reaction.

Nevertheless, (1), viewed as an empirical relation, serves the purpose of describing the rate and has otherwise the same usefulness as the analogous equation in chemical kinetics.

An explanation of the observed tail-off is presented on the basis of three independent processes: (a) the confining effect of the piston in the vessel, due to friction, (b) the effect of nucleation, and (c) the effect of introduced strain energy. Bridgman [1915] studied solid-solid transformation rates with his vessel held at constant volume, and the tail-off of his curves resulted primarily from the return of pressure to near that at the equilibrium boundary as the transition proceeded. Although the present experiments were maintained as nearly as possible at constant pressure, it is quite possible that some of the tail-off observed could result from pressure changes coming from retarded piston movement in the vessel.

That such a process cannot account for all of the tail-off is shown by the rate curves obtained from the high-temperature stage (Figure 4, C and D). In this arrangement the samples were also compressed pellets, but were lying on the heating strip of the stage open to the atmosphere. Therefore, it is proposed that much of

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 \rightarrow 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

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

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 $1/T^\circ\text{K}$ versus $-\log K$, and $1/T^\circ\text{K}$ versus \log time for 40% transformation. The activation energy for the aragonite \rightarrow 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 \rightarrow 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

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

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

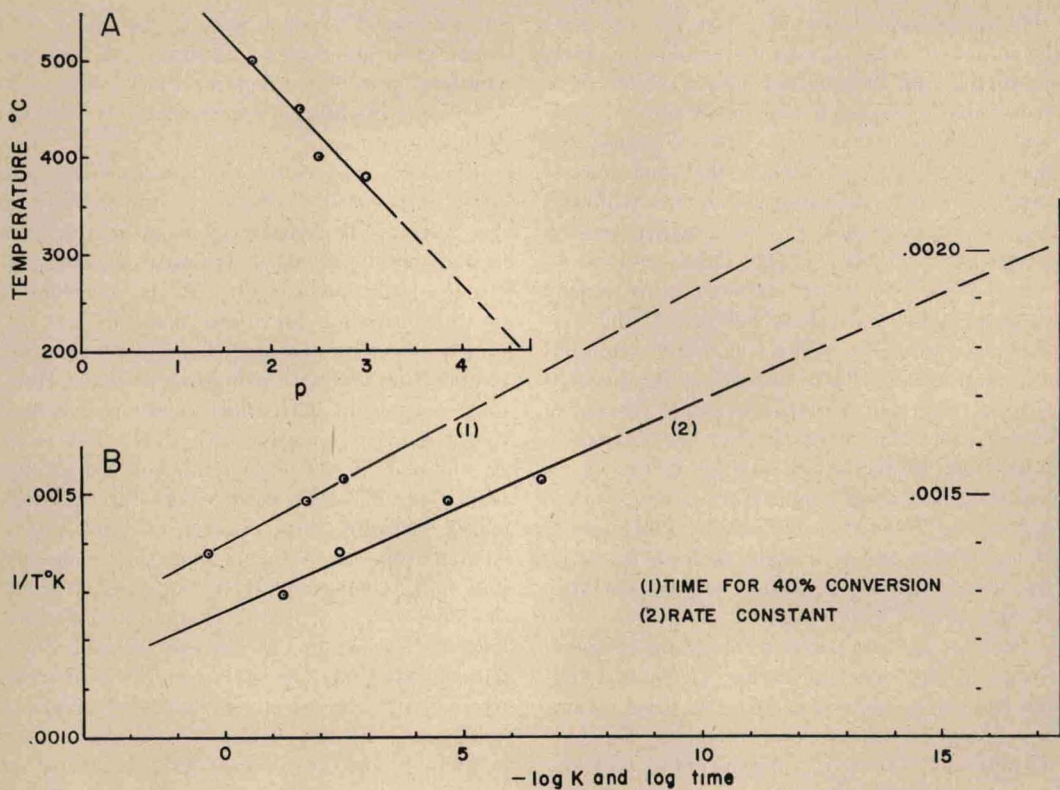


Fig. 5. A; plot of the exponent p of equation 1 versus $T^{\circ}\text{C}$ for Kamsdorf aragonite calcite at 1 bar (beryllium pressure vessel). B; plot of $-\log K$ and \log time for 40% conversion versus $1/T^{\circ}\text{K}$ for Kamsdorf aragonite \rightarrow calcite at 1 bar (beryllium pressure vessel).

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° . 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

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.

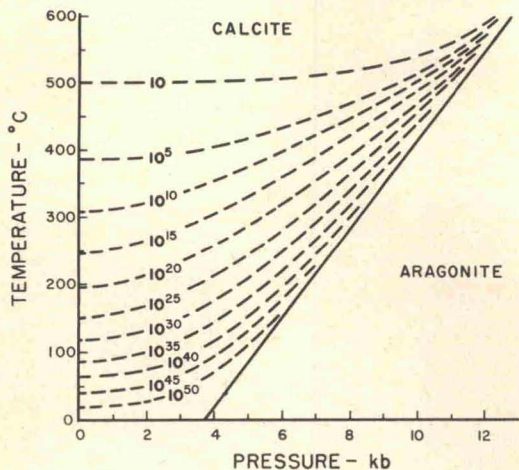


Fig. 6. Isochrons (lines of equal time) for 99% conversion of Kamsdorf aragonite \rightarrow calcite plotted in the calcite stability field. Isochron values are in minutes.

factor responsible for the difference in the gradient obtained by Brown et al. and by us appears to be the magnitude of the pressure effect on the transition. The former authors allow only a factor of 10 for a pressure effect 1 kb below the phase boundary.

At best such calculations are only approximate inasmuch as they rest on the assumption that the Franciscan rocks were dry during unloading and that the changing of pressure-temperature conditions of the aragonite material down the geothermal gradient (i.e., rate of unloading) was slow enough to allow sufficient time at the higher temperatures for transformation to take place.

Of further interest is the fact that the rates of the calcite \rightarrow aragonite transformation at 375 to 405°C and 15 \pm 1 kb are of the same order of magnitude as those for the reverse transformation at 400°C and 1 bar. It is apparent that the amount of overstepping of the equilibrium pressure has roughly the same effect in rate acceleration as the degree of understepping. One might also expect (although on a less certain experimental basis) that a set of isochrons similar to that proposed for the calcite field is applicable to the aragonite field.

Acknowledgments. We acknowledge the helpful comments and suggestions of Drs. Daniel Kivelson, K. D. Watson, N. Gary Lane, W. Gary Ernst, and Ronald L. Shreve.

This research program was supported in part by grants from the National Science Foundation.

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(Manuscript received July 24, 1964;
revised September 12, 1964.)