



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	$p$	$K$ (%) <sup>1-p</sup> /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†	$1.2 \times 10^{-8}$		B
3	1	A-C	380	0.001	52	632	3.0	$2.3 \times 10^{-7}$	0.47	B
4	1	A-C	400	0.001	74	284	2.5	$2.1 \times 10^{-5}$	0.23	B
5	1	A-C	450	0.001	86	18	2.3	$3.8 \times 10^{-3}$	0.18	B
6	1	A-C	500	0.001	96	9	1.8	$5.8 \times 10^{-2}$	0.26	B
7	2	A-C	400	$8 \pm 1$	53	1143	7.0	$7.0 \times 10^{-15}$	0.11	B
8	2	A-C	450	$8 \pm 1$	34	112	10.0	$8.1 \times 10^{-20}$	0.19	B
9	2	A-C	500	$10 \pm 1$	92	25	1.5	$3.7 \times 10^{-2}$	0.21	B
10	3	C-A	375	$15 \pm 1$	63	95	3.0	$3.8 \times 10^{-6}$	0.20	B
11	3	C-A	405	$15 \pm 1$	73	678	3.0	$1.2 \times 10^{-5}$	0.17	B
12	4	A-C	450	0.001	97	48	1.2	$4.3 \times 10^{-2}$	0.12	S
13‡	4	A-C	450	0.001	95	200	1.8	$4.2 \times 10^{-3}$	0.23	S
14§	4	A-C	450	0.001	92	99	1.5	$5.4 \times 10^{-3}$	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  $15 \pm 1$  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<sub>3</sub>-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