The Arrhenius equation:

$$\frac{d \ln k}{d T} = \frac{E_a}{RT^2}$$

can be used with the data from experiments 71, 91 and 80 to evaluate the variation of the rate constants with temperature, and to calculate the Arrhenius apparent energy of activation (E_a).

Figure 7 is a plot of the Arrhenius equation using data from experiments nos. 70, 71, 91, 80, and 81. The pressure (2000 psi) and the time (2 hours) were common to all experiments. The temperatures are 535°C, 605°C, 735°C, 790°C, and 870°C respectively. The apparent activation energy is calculated from the linear portion of the plot.

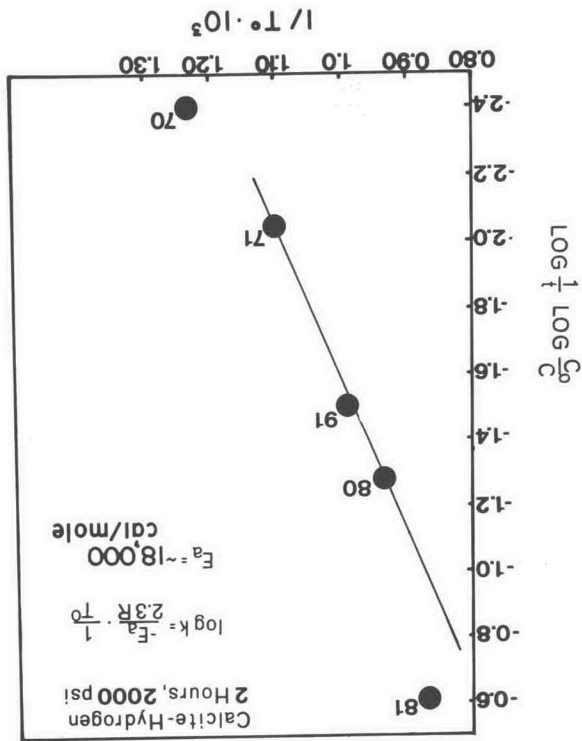The Arrhenius equation: $d \ln k/dT = E_a/RT^2$, because E_a is constant,

Fig. 7. Plot of $\log(1/t \log C_0/C)$ or $\log k$ against the reciprocal of the absolute temperature for experiments numbered 70, 71, 92, 80, and 81. These experiments were run at 2000 psi (H_2); 2 hours; at 535, 605, 735, 790, and 870° respectively. The Arrhenius activation energy calculated from the slope of experiments 71, 91, and 80 is 23,000 cal/mole.

can be integrated with respect to T to give $\ln k = -E_a/RT + C$. This latter form was used with the data from experiments 71, 91, and 80 to calculate the Arrhenius apparent activation energy (E_a). This activation energy is 18,000 cal/mole.

TABLE 3. DATA USED IN THE EVALUATION OF THE ACTIVATION ENERGY IN FIG. 7

Exp. No.	°C	$1/T°$	C_0	C	C_0/C	$\log C_0/C$	$\dfrac{1}{t}\log C_0/C$	$\log\left(\dfrac{1}{t}\log\dfrac{C_0}{C}\right)$
70	535	1.23×10^{-3}	43.7	43.0	1.02	0.0086	0.004	−2.40
71	605	1.14×10^{-3}		43.0	1.04	.0170	.008	−2.05
91	735	0.99×10^{-3}		37.8	1.16	.0645	.032	−1.50
80	790	$.94\times10^{-3}$		34.5	1.27	.1038	.052	−1.28
81	870	$.87\times10^{-3}$		16.3	2.68	.4281	.214	−0.61

The relation between the rate constant and the initial and final concentration of a reactant in a first-order reaction is as follows:

$$k = \frac{1}{t}\ln\frac{C_0}{C};$$

and the activation energy can be evaluated from Figure 7.

The slope was determined by using only the information from experiments 71, 91, and 80. Experiment 70 was excluded because of the analytical uncertainty in determining so small a change in the amount of reacted calcite. Experiment 81 was excluded because of the likelihood of a change in the behavior of the system at higher temperatures.

The digression from linearity of the sample at 870°C may result from the interaction of a competing reaction. The competing reaction may be either or both the thermal dissociation of calcite and the pyrolysis of methane.

Usually a homogeneous reaction has a higher activation energy and so is favored at high temperatures, whereas the heterogeneous reaction predominates at lower temperatures. The pyrolysis methane decomposition may also effect the calcite-hydrogen reaction rate. Britton, Gregg and Winsor (1952a) and Britton Gregg, Winsor and Willing (1952) on the basis of a study of the thermal decomposition of calcite in vacuum, concluded that the rate of dissociation was proportional to the area of the interface. Our studies support the conclusion that the calcite-hydrogen reaction is surface dependent.

In earlier work where a single cleavage rhombohedron was used for the calcite charge, it was common to recover a core of unreacted calcite enveloped by a cohesive rim of calcium hydroxide. Many of these samples