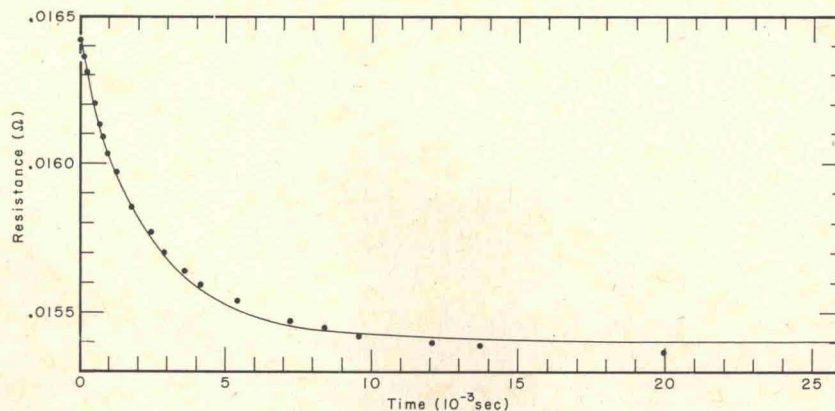FIG. 6. Resistance changes during anneal at 286°C and 1 kbar of sample first equilibrated at 368°C. The curve is calculated to give the best fit to the datum points as described in the text.

at constant temperatures ranging between 247° and 290°C under various pressures. During this second anneal, the degree of long-range order within the domains increases with no significant change in the domain size itself. Thus, changes in the sample resistance, R, are directly related to changes in the long range order parameter, S, and are expected to follow the equation

$$(R-R_0)/(R_e-R_0) = \coth(\alpha t+\beta).$$

To find the pressure- and temperature-dependence of the rate constant α from this equation, R_0 and R_e must be determined as a function of T and P. R_e is the final resistance of the sample held until the homogeneous ordering is completed at the temperature and pressure of interest. The determination of R_0 as a function of temperature and pressure is more difficult. The procedure used is given in the Appendix. Essentially, it consists of relating the order-dependent resistance of a sample to the lattice parameter and then extrapolating to the value of the lattice-parameter characteristic of the fully ordered material to find R_0 at 25°C and 1 atm. The temperature and pressure coefficient of resistance of a highly ordered sample are then measured and used to find $R_0(T, P)$.

The procedure for measurement of the ordering rate is to first set up a quenched sample in the anvils and measure its resistance at room temperature and pressure. Then a pressure of a few hundred bars is applied and T raised to 100°C. At this temperature the sample is brought to the pressure to be used in the experiment; it is then rapidly heated and, when the temperature is stabilized (usually within 45 min), the resistance is measured as a function of time until the equilibrium resistance is attained. At the temperatures and pressures used, this may require a time between a few hours and a few days. During this anneal T is held to ±0.5°C and P to within ±40 bars.

The resistance changes during a typical ordering experiment are shown in Fig. 6. To the datum points shown, Eq. (1) must be fitted. In making this fit, allowance must be made for possible errors in the

determination of R_0 and R_e. This was done by means of a computer program which compares Eq. (1) with the data for the following range of the variables R_0, R_e, and α:

$$\Delta R_0 = 1.1R_0 \quad \text{to} \quad 0.7R_0,$$

$$\Delta R_e = 1.0R_e \quad \text{to} \quad 0.9R_e,$$

$$\Delta \alpha = 3.0\alpha \quad \text{to} \quad 0.3\alpha.$$

The starting points for the computation are the measured R_0 and R_e and a value of α estimated from room-pressure data. As successively better fits are obtained, the interval of variation of the three parameters is made smaller until, at the final fit, the intervals are

$$\delta R_e = 4 \times 10^{-5} R_e,$$

$$\delta R_0 = 1.7 \times 10^{-5} R_0,$$

$$\delta \alpha = 6 \times 10^{-4} \alpha.$$

At this interval size computational errors are negligible compared to experimental errors.

Two series of kinetic experiments were done. In one, a constant pressure of 900 bars was used and the ordering temperature was varied between 247° and 289°C; in the other, the temperature was 286°C and pressure ranged from 1 to 14 kbar. Rate constants from the first series are shown in Fig. 7 and are seen to fit Eq. (2). The activation energy for ordering obtained from this plot is 1.9±0.2 eV. This may be compared with the value of 2.03 eV obtained by Feder, Mooney, and Nowick,[5] and the 1.95-eV value found by Goering and Nowick[14] by an internal friction experiment.

The results of the second series of measurements, in which a series of pressures and one temperature were used, are shown in Fig. 8. It is seen from this figure that the data fit an equation of the form of Eq. (3). The slope of the line drawn through the points yields a total activation volume for ordering of 6.8±1 cm³/mole or $(11\pm2)\times10^{-24}$ cm³/atom.

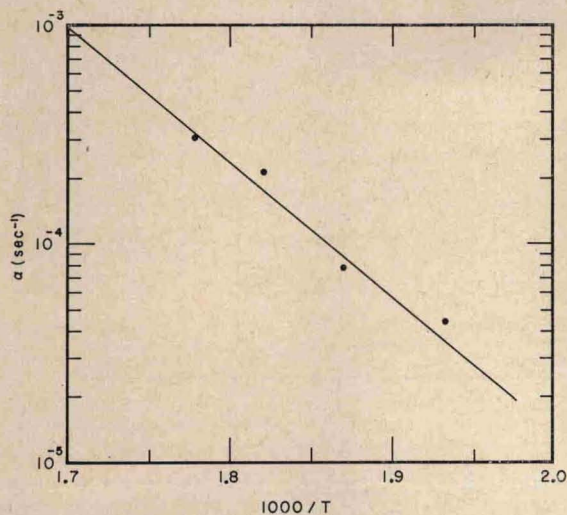[14] W. Goering and A. S. Nowick, Trans. AIME 105, (1958).

FIG. 7. Variation of the rate constant α with temperature at 900 bars. The slope of the straight line corresponds to an activation energy of 1.9 eV.

DISCUSSION

The measured room-pressure values of V_t and H_t indicate an initial slope of the T_c vs P curve of 1.3°K/kbar. An old measurement by Wilson[15] gives an initial slope of 1.2°K/kbar. A smooth curve drawn through the data points in Fig. 5 would have a slope of 2.1°K/kbar at zero pressure. An increase in dT_c/dP
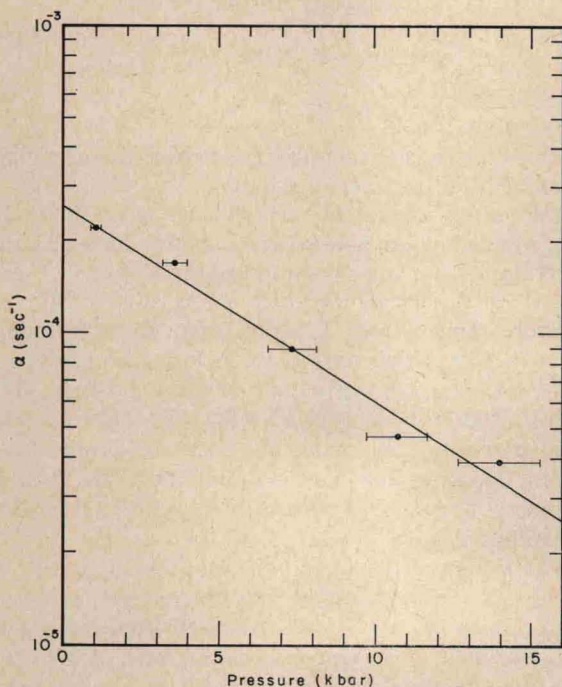

FIG. 8. Variation of the rate constant α with pressure at 286°C. The slope of the line corresponds to an activation volume of 6.8 cm³/mole of atoms.

[15] T. C. Wilson, Phys. Rev. **56**, 598 (1939).

at higher pressures is expected because of the increase in T_c, but allowance must also be made for the pressure variation of V_t and H_t. The change in V_t with pressure assuming a constant degree of long range order at T_c can be estimated by using Siegel's[16] measurements of the elastic constants of the ordered and disordered phases at high temperature to compute the compressibilities of the two phases. A correction for the pressure-dependence of the elastic constants can be estimated from Lazarus'[17] data on the pressure-dependence of the elastic constants of Cu and Au. At 21 kbar, V_t is reduced from 2.25×10^{-2} to 1.94×10^{-2} cm³/mole of atoms. This decrease in V_t almost compensates the increase in T_c so that dT_c/dP would remain about constant (the change in H_t at 21 kbar due to PV_t is negligibly small). The form of the curve in Fig. 5 must result, then, from changes in V_t and H_t resulting from a shift in the amount of long-range order just below T_c and short-range order just above T_c as the pressure is increased.

TABLE I. Activation energies and volumes.

	Q	V^*
Ordering kinetics	2.0 eV	6.8 cm³/mole
Anelastic, Cu_3Au[a]	1.95	
Diffusion, Au in Cu[b]	1.95	
Diffusion, Au in Au[c]	1.81	7.2
Diffusion, Au in Ag–Au alloy[d]		7.5
Diffusion, Ag in Ag[e]		9.2
Anelastic, Ag–Zn alloy[f]		5.4
Atomic radii		
Au 1.44 A Ag 1.44 A		
Cu 1.28 Zn 1.37		

[a] See Ref. 14.   [d] See Ref. 20.
[b] See Ref. 18.   [e] See Ref. 21.
[c] See Ref. 19.   [f] See Ref. 22.

The results in Fig. 8 show that Eq. (3) gives an adequate representation of the pressure-dependence of the ordering rate below T_c. Since V_t is about 0.03 cm³/mole, the term $1/2 PV_t$ can be neglected in comparison with PV^* in Eq. (3). Within the accuracy attained in these experiments, no pressure variation in V^* could be detected; more accurate determination of the sample pressure would be required for this purpose.

The values of Q and V^* found in these experiments are compared with other related quantities in Table I. Change in the state of order in Cu_3Au involves thermally activated movements of both the Au and the Cu atoms; the slowest-moving species will determine the

[16] S. Siegel, Phys. Rev. **57**, 537 (1940).
[17] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[18] A. B. Martin, R. D. Johnson, and F. Asaro, J. Appl. Phys. **25**, 364 (1954).
[19] R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, Phys. Rev. **137**, A613 (1965).
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[21] C. T. Tomizuka, R. C. Lowell, and A. W. Lawson, Bull. Am. Phys. Soc. II**5**, 181 (1960).
[22] G. W. Tichelaar and D. Lazarus, Phys. Rev. **113**, 438 (1959).