

TABLE I. Variation of diffusivity of Fe⁵⁹ with hydrostatic pressure at 944.5 °C.

Pressure (kbar)	<i>D</i> , (cm ² /sec)
0	(5.52 ± 0.15) × 10 ⁻¹¹
1.44 ± 0.01	(5.33 ± 0.06) × 10 ⁻¹¹
3.10 ± 0.01	(4.94 ± 0.09) × 10 ⁻¹¹
4.55 ± 0.03	(4.53 ± 0.07) × 10 ⁻¹¹

out in an argon atmosphere using an internally heated high-pressure vessel.⁶ The thermocouple was cemented inside a FeCo dummy piece in order to correctly measure the temperature of the sample. The temperature was controlled automatically and was constant to approximately ± 0.5 °C. A pressure correction of 0.5 °C/kbar was assumed for the Pt-Pt-10 at. % Rh thermocouple.⁶ The pressure was maintained constant usually to 1% or better over the duration of the 24-h runs. The zero-pressure anneal was carried out in a vacuum furnace using a welded specimen identical to the pressure specimens.

The samples were analyzed by the standard techniques of lathe-sectioning and counting, with appropriate corrections made for welding and warm-up time, equipment drifts, tracer decay, and background activity. The sections were contained in thin cellulose acetate butyrate vials and counted with an NaI (Tl) well-type scintillation detector.

The penetration profiles [plots of log (specific activity) versus penetration distance squared] for diffusion of Fe⁵⁹ in equiatomic FeCo alloys at 944.5 °C and 0, 1.44, 3.10, and 4.55 kbar are shown in Fig. 1. The diffusion coefficients are given in Table I and shown graphically in Fig. 2. The largest single source of error in the *D* values is uncertainty in the temperature measurements. (A 2 °C error in temperature results in about a 4% error in *D*.) Other sources of error, such as weighing, counting, anneal time, etc., were of the order of 1% or less combined, so that we estimate the uncertainties in *D* values to be approximately 3-4%.

The activation volume is calculated according to^{4,7}

$$V = -RT \frac{\partial \ln D}{\partial P} + RT \gamma_G K_T, \quad (1)$$

where γ_G is the Grüneisen constant, K_T is the isothermal volume compressibility, and the other terms have their usual meanings. The second term of Eq. (1) is small compared to the first, and will be discussed below. From the first term of Eq. (1), the activation volume is computed to be 4.34 cm³/mole, from a least-squares determination of the slope of Fig. 2. The standard deviation in the

slope, considering just the data points themselves, is $\sigma(\Delta V) = 0.35$ cm³/mole. However, allowing for a reasonable temperature uncertainty of ± 1.5 °C, the corresponding uncertainty in *D* leads to a variance in the slope of $\sigma(\Delta V) = 0.89$ cm³/mole. It is considered that the small variance in the first instance is probably fortuitous, and that the latter figure more realistically characterizes the experimental data.

The second term of Eq. (1) is estimated to be approximately 0.04 cm³/mole, based on the Grüneisen relation $\gamma_G K_T = 3\alpha V/C_v$,⁸ and available values or estimations of the thermal expansion,⁹ specific heat,¹⁰ and compressibility.¹¹ The molar volume (at room temperature) is determined to be 7.09 cm³/mole, based on the measured density of these alloys (8.10 g/cm³) and the average atomic weight of Fe and Co. The molar volume at 944.5 °C is then approximately 7.33 cm³/mole. The final value of the activation volume is thus

$$\begin{aligned} \Delta V &= 4.38 \pm 0.89 \text{ cm}^3/\text{mole} \\ &= 0.60 \pm 0.12 V_M, \end{aligned} \quad (2)$$

where V_M is the molar volume.

The value of $\Delta V/V_M = 0.60$ determined in this work may be compared with corresponding values found in other bcc metal systems: 0.52 in Na,¹² 0.28 in Li,¹³ and 0.45-0.60 in the α phase of the Fe-V system.¹⁴ In the latter work, the activation volume for chemical interdiffusion was observed

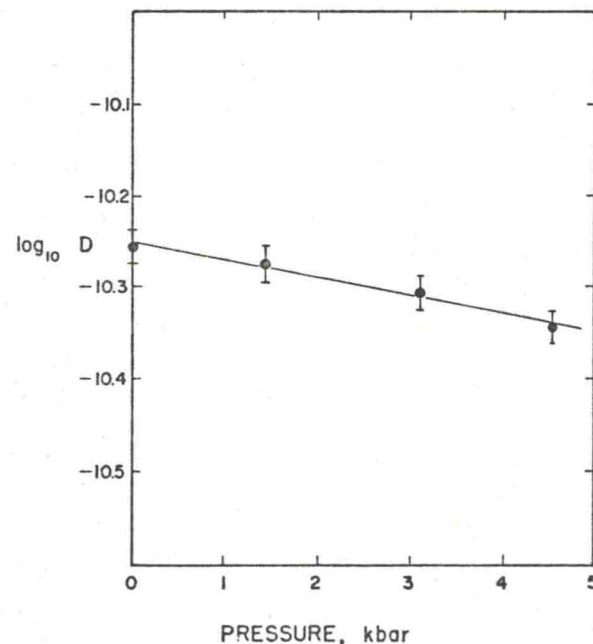


FIG. 2. Diffusion coefficient vs pressure for diffusion of Fe⁵⁹ into equiatomic FeCo alloys at 944.5 °C.