

Solute Diffusion in Alpha- and Gamma-Iron

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The diffusion rates of chromium, vanadium, and hafnium in α - and γ -Fe have been determined by radiotracer techniques. The results are (in sq cm sec⁻¹):

	α -Fe	γ -Fe
Chromium	$D = 8.52 \exp\left(\frac{-59,900}{RT}\right)$	$D = 10.80 \exp\left(\frac{-69,700}{RT}\right)$
Vanadium	$D = 3.92 \exp\left(\frac{-57,600}{RT}\right)$	$D = 0.25 \exp\left(\frac{-63,100}{RT}\right)$
Hafnium	$D = 1.31 \exp\left(\frac{-69,300}{RT}\right)$	$D = 3600 \exp\left(\frac{-97,300}{RT}\right)$

The differences in diffusion rates are discussed in terms of the compressibility of the diffusing atom. Diffusion of chromium in γ -Fe was also measured by a microprobe analysis technique. The result is:

$$D = 4.08 \exp\left(\frac{-68,500}{RT}\right)$$

Comparison is made between diffusion analysis by tracer techniques and by electron probe microanalysis.

BECAUSE of its technological importance, it is necessary that the diffusion rates of all possible alloying elements in iron be known. This paper is a report on the diffusion rates of chromium, vanadium, and hafnium in α - and γ -Fe. The study was part of a larger program, involving the investigation of diffusion in bcc iron alloys.¹ In order to study diffusion in α -Fe over as large a temperature range as possible, results were also obtained on an alloy, Fe-2 pct V; Lai and Borg² have already shown that there is no systematic difference between diffusion in pure iron and in an alloy of similar composition to the one used in the present investigation. Therefore, the results for impurity diffusion in Fe-2 pct V should be synonymous with diffusion in pure α -Fe, within experimental error. Most measurements were made using tracer techniques; additional measurements used the electron probe microanalyzer for chromium diffusion.

EXPERIMENTAL PROCEDURE

High purity iron and an Fe-2 pct V alloy were supplied by the British Iron and Steel Research Association. The analyses of these materials are given in Table I. Further purification was carried out by annealing 8 cm long sections in flowing dry hydrogen for 2 days at 1000°C, followed by decarburization at 890°C in flowing moist hydrogen for 7 days. Specimens, machined from these sections (5.50 by 8.0 mm) were polished by holding them in a block similar to that of Eisen and Birchenall.³ They were then further an-

nealed (at 1000°C for α -Fe studies and at 890°C for γ -Fe studies) for 7 days in flowing dry hydrogen in order to eliminate machining strains and to give a grain size of between 2 and 3 μ m. Prior to the deposition of the isotope each specimen was given a final polish on a 1 μ m diamond wheel. Immediately prior to plating each specimen was etched in 2 pct nital to remove any deformed layer which may have been introduced during final polishing.

The characteristics of the isotopes Cr⁵¹, V⁴⁸, and Hf¹⁸¹ are given in Table II. The isotopes were supplied by United Kingdom Atomic Energy Authority, Amersham. Cr⁵¹ was supplied as sodium chromate; V⁴⁸ and Hf¹⁸¹ as the chloride in HCl. All solutions were carrier free. Chromium is deposited only from chromic acid; sodium chromate was therefore converted into chromic acid by the addition of concentrated H₂SO₄. The other isotopes were deposited from the solution as supplied. The time of deposition was approximately

Table I. Composition of Pure Iron and Fe - 2 Pct V

Wt Pct	V	C	N ₂	O ₂	Al	Si	S
Pure iron	—	0.003	0.0014	0.0014	0.003	0.001	0.005
Fe-2 pct V	2.15	0.003	0.0014	0.0014	0.003	0.001	0.005

Table II. Characteristics of the Isotopes Cr⁵¹, V⁴⁸, and Hf¹⁸¹

Isotope	Half Life	Radiation Emitted	Energy Levels of Emitted Rays, MeV
Cr ⁵¹	27.8 days	γ and X-rays	X - 0.005 V X-rays γ - 0.32
V ⁴⁸	16 2 days	β and γ rays	β - 0.7 γ - 1.0, 1.31, 2.25
Hf ¹⁸¹	42.5 days	β and γ rays	β - 0.41 γ - 0.13, 0.35, 0.48

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20 min for V⁴⁸ and Cr⁵¹ and 2 to 3 hr for Hf¹⁸¹. The thickness of the deposited isotopes was <0.1 μm.

Diffusion anneals were carried out in a platinum wound furnace under an atmosphere of flowing dry pure hydrogen. All samples were encapsulated in foils of pure iron and in the case of hafnium diffusion, the specimens were annealed in pairs with a thin (500 μm) iron washer separating the two plated faces, minimizing evaporation of the isotope. Temperatures were measured with Pt-Pt 13 pct Rh thermocouples to better than ±2° at 1450°C and ±1° at 1000°C. No heating or cooling corrections were necessary. Diffusion runs were carried out over the following temperature ranges: Cr—797° to 877°C and 960° to 1396°C; V—1004° to 1447°C and 1102° to 1356°C; and Hf—1098° to 1384°C and 1098° to 1353°C.

Prior to sectioning and analysis each specimen was turned in a lathe to remove 500 μm from their diameters. This eliminated any tracer which had been transported by surface diffusion around the edge of the specimen.

Penetration curves were obtained using the residual activity technique. In this method successive parallel layers of metal are progressively ground off. The activity of each new surface is then measured. Standard equipment was used to measure the radioactivity. A particular radiation of each isotope was isolated using a pulse height analyzer and amplitude discriminator. The absorption coefficient for that particular radiation was calculated from published data. Corrections for isotope decay were unnecessary. All specimens were counted for 10,000 counts. This ensured that the count rate was representative of the surface under examination. Weighings were carried out in a microbalance, capable of measuring to 0.01 μkg. The densities of iron and Fe-2 pct V were determined using Archimedes principle, with ethylene dibromide as a reference liquid, against pure tin standards.

Procedure for Probe Microanalysis

Specimen preparation and annealing were identical with those for tracer analysis. The thickness of the chromium deposit was estimated as <0.5 μm.

After annealing each specimen was sectioned at 90 deg to the plated face. This cut face was then polished and examined in the electron probe microanalyzer. A concentration curve was determined by taking point counts at regular intervals away from the plated surface until the count rate was only three times the background rate. The diffusion profile thus determined is exactly comparable to the tracer technique and can be solved by using Eq. [2].

TREATMENT OF RESULTS

Residual activity measurements involve surface counting. It is therefore necessary to consider contributions to the measured activity from atoms below the surface. Gruzin⁴ has derived the following equation, which is applicable to this technique

$$I - \frac{1}{\mu} \frac{\partial I}{\partial x} = \frac{K}{(\pi Dt)^{1/2}} \exp\left[-\frac{x^2}{4Dt}\right] \quad [1]$$

where

I is the measured activity

μ is the linear absorption coefficient

x is the distance from the interface

K is a constant

D is the diffusion coefficient, and

t is the time of the anneal.

If μ is very large and penetration is deep, Eq. [1] becomes

$$\ln I = -\frac{x^2}{4Dt} + C_1 \quad [2]$$

where C_1 is a constant. Eq. [2] is identical to the thin film solution of Fick's second law.⁵ Therefore, for low energy radiation, Eq. [2] is applicable (*e.g.*, Ni⁶³) without it being necessary to correct for absorption. If μ is very small, Eq. [1] becomes

$$\ln -\frac{\partial I}{\partial x} = -\frac{x^2}{4Dt} + C_2 \quad [3]$$

where C_2 is also a constant. Absorption corrections are also therefore unnecessary when Eq. [3] is used for high energy radiation (*e.g.*, Co⁶⁰). However, in many cases Eq. [2] is applicable, but $(1/\mu)(\partial I/\partial x)$ should not be neglected if an accurate value of D is to be quoted. Since in these circumstances Eq. [2] is obeyed, and penetration is deep, differentiation of this equation gives

$$\frac{\partial I}{\partial x} = -\frac{xI}{2D't} \quad [4]$$

where D' is the approximate diffusion coefficient from Eq. [2]. Substituting Eq. [4] in Eq. [1] gives

$$\ln \left[I + \frac{1}{\mu} \frac{xI}{2D't} \right] = -\frac{x^2}{4Dt} + C \quad [5]$$

This process may be repeated for increased accuracy if necessary. All activity readings were corrected in this manner. A plot of $\ln \left[I + (1/\mu)(xI/2D't) \right]$ vs x^2 will yield a straight line, the slope of which is $-1/4Dt$. Diffusion obeys the Arrhenius relationship

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

The quantities Q (activation energy) and D_0 (frequency factor) can therefore be obtained by plotting $\ln D$ vs $1/T$. Eqs. [6] to [23] are of this form.

Table III. Experimental Values of Activation Energy and Frequency Factor for Solute Diffusion in α - and γ -Fe

		Q , cal per mole	D_0 , sq cm per sec	Equation
Fig. 1	Chromium in paramagnetic α -Fe	59900(± 1600)	8.52 $\begin{pmatrix} +3.20 \\ -2.33 \end{pmatrix}$	[6]
	Vanadium in Fe-2 pct V	57600(± 1300)	3.92 $\begin{pmatrix} +0.82 \\ -0.68 \end{pmatrix}$	[7]
	Hafnium in Fe-2 pct V	69300(± 3700)	1.31 $\begin{pmatrix} +0.94 \\ -0.55 \end{pmatrix}$	[8]
Fig. 2	Chromium in γ -Fe	69700(± 1700)	10.80 $\begin{pmatrix} +3.35 \\ -2.56 \end{pmatrix}$	[9]
	Vanadium in γ -Fe	693100(± 2200)	0.28 $\begin{pmatrix} +0.10 \\ -0.08 \end{pmatrix}$	[10]
	Hafnium in γ -Fe	97300(± 2600)	3600 $\begin{pmatrix} +1600 \\ -1100 \end{pmatrix}$	[11]

RESULTS

The results of the present work are presented in Figs. 1, 2, and 3. Q and D_0 values, Eqs. [6] to [11], are given in Table III.

The result calculated from electron probe micro-analysis is

Chromium in γ -Fe

$$D = 4.08 \begin{pmatrix} +1.89 \\ -1.29 \end{pmatrix} \exp \left(-\frac{68,500 \pm 2500}{RT} \right) \quad [12]$$

A comparison of the tracer and probe results is shown in Fig. 3. The activation energy and frequency factor and the errors in these values were calculated by the method of least squares.

Lai and Borg² have shown that iron diffusion in Fe-2 pct V is synonymous with self diffusion. Time considerations precluded a study of vanadium diffusion in α -Fe in order to verify this hypothesis for impurity diffusion. However, further diffusion data, obtained in the Fe-V system, confirms the validity of this assumption.¹

DISCUSSION

Although these appear to be the first results to be published of diffusion of these elements in iron, (with the exception of chromium diffusion in α -Fe⁶ and hafnium diffusion in γ -Fe⁷), it is possible to compare these results with those for diffusion of transitional elements in α - and γ -Fe, as given in Table IV, Eqs. [13] to [23]. The earlier work of Sparke *et al.*⁷ for hafnium diffusion in γ -Fe, Eq. [23], was calculated from only three points. It was therefore felt that a re-determination of this equation would be desirable. Although Eqs. [11] and [23] differ markedly, they both indicate that diffusion of hafnium in γ -Fe is extremely slow by comparison with other transitional metals.

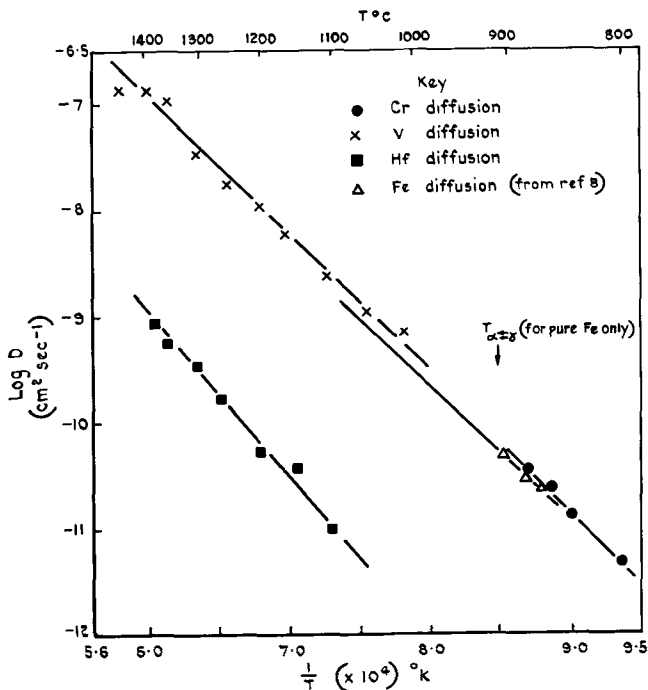


Fig. 1—Log D plotted as a function of T^{-1} for Cr, V, Hf, and Fe diffusion in α -Fe. (Chromium and iron diffusion in pure iron; vanadium and hafnium diffusion in Fe-2 pct V).

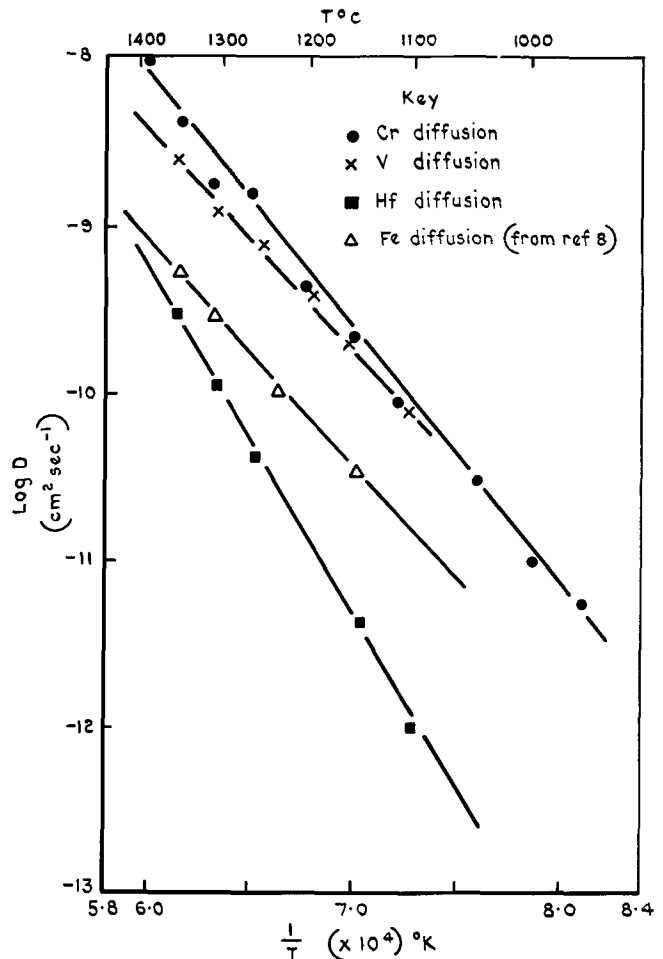


Fig. 2—Log D plotted as a function of T^{-1} for Cr, V, Hf, and Fe diffusion in γ -Fe.

An explanation for this is offered later. The agreement between Eqs. [6] and [14] is extremely good even allowing for the Curie point effect.

A comparison of Eqs. [6] to [12] with Eqs. [13] to [23] shows that the present results are well in accord with previous work (excluding hafnium diffusion in γ -Fe). Eqs. [6] to [12] and [14], [22], and [23] describe the diffusion of electronegative elements while Eqs. [13] to [21] describe the diffusion of electropositive elements. No systematic differences in behavior are noticeable. A discontinuity in diffusion rates at the $\alpha \rightarrow \gamma$ transformation was obtained only for chromium. Diffusion rates decreased approximately 2 orders of magnitude. Similar changes have been observed previously.^{7-9, 13}

Calculations of the changes in activation energy for impurity diffusion have been presented by Swalin¹⁴ and Lazarus.¹⁵ Approximations are involved in both approaches. Swalin¹⁴ considers the change in activation energy to be due to differences in atomic size and elastic properties of the solute and solvent atoms. Lazarus¹⁵ ignores these differences in size, arguing that atoms are electronic configurations and that changes in diffusion rates are due to changes in electronic configurations. Both theories have been found to be too simple to explain diffusion in transitional metals on many occasions.¹⁶⁻¹⁸ Eqs. [6] to [23] confirm these conclusions. Calculations on Lazarus'

principles immediately run into difficulty because the Fermi-Thomas equation cannot be determined with any accuracy. Neither can the screening parameter¹⁸ be calculated accurately. In the absence of data to fit Swalin's theory, the change in activation energy can be explained qualitatively as being due to the variations in compressibility between the diffusing atom and the solvent atom (in this case—iron). Gibbs and Askill¹⁹ have illustrated this dependence of Q on compressibility for self-diffusion. The present results allow this idea to be extended to solute diffusion. Fig. 4 illustrates the plot of inverse compressibility and Q_{impurity} vs transitional element for diffusion in α - and γ -Fe (the value for iron being the self-diffusion

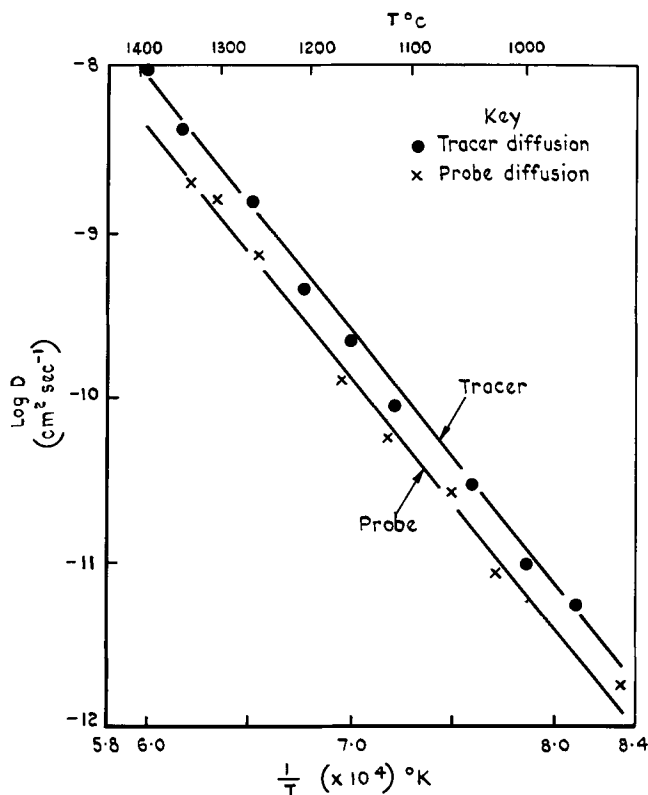


Fig. 3—Log D plotted as a function of T^{-1} for chromium diffusion in γ -Fe (●—tracer diffusion; ×—probe diffusion).

Table IV. Previous Results for Diffusion in α - and γ -Fe

	Q , cal per mole	D_0 , sq cm per sec	Ref.	Eq.
Self-diffusion in paramagnetic α -Fe	57,300	2.0	8	[13]
Chromium diffusion in ferromagnetic α -Fe	57,500	2.53	6	[14]
Cobalt diffusion in paramagnetic α -Fe	61,400	6.4	9	[15]
Nickel diffusion in paramagnetic α -Fe	61,900	9.9	10	[16]
Copper diffusion in paramagnetic α -Fe	57,000	0.57	11	[17]
Gold diffusion in paramagnetic α -Fe	62,400	31	10	[18]
Self-diffusion in γ -Fe	64,000	0.2	8	[19]
Cobalt diffusion in γ -Fe	72,900	1.25	12	[20]
Nickel diffusion in γ -Fe	67,000	0.77	13	[21]
Niobium diffusion in γ -Fe	82,300	530	7	[22]
Hafnium diffusion in γ -Fe	113,000	9×10^4	7	[23]

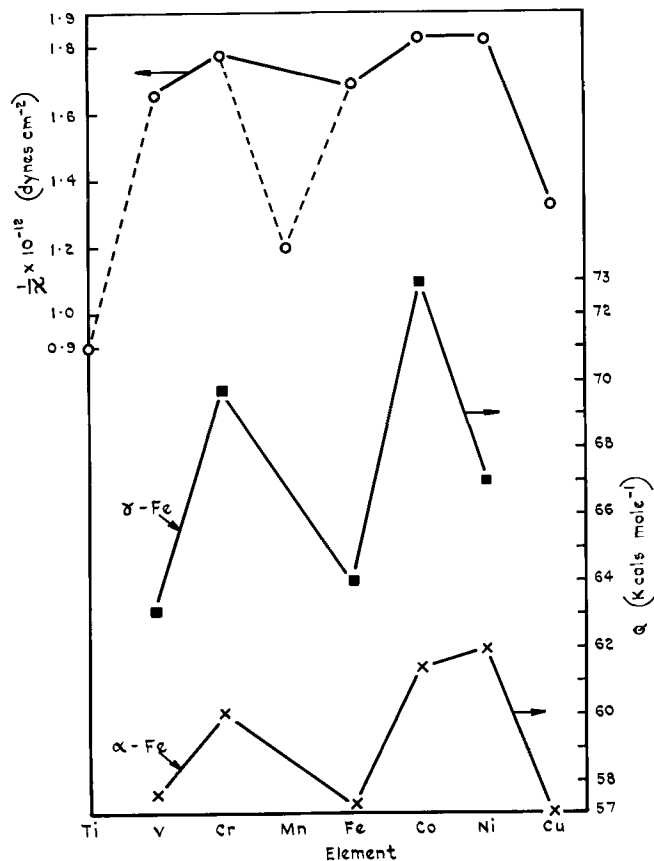


Fig. 4—Variation of activation energy and compressibility with atomic number. [×—diffusion in α -Fe; ■—diffusion in γ -Fe; ○—inverse compressibility ($1/\chi$)] (compressibility data from Refs. 30 and 31).

Q). This figure therefore schematically predicts Q values on the basis of the compressibility of the diffusing atom. There is no value for manganese or titanium tracer diffusion in α -Fe available at present, but Fig. 4 predicts that Q should be approximately 50 to 53 kcal per mole. Diffusion studies on Fe-Ti alloys¹ suggest that Q_{Ti} is in this range, *i.e.*, approximately 50 kcal per mole. The curve for diffusion in γ -Fe is not so dependent on $1/\chi$. Fig. 4 may therefore only be applicable to bcc metals, the looser packing of the bcc lattice allowing the compressibility of the diffusion atom during vibration to dominate other effects. No such relationship exists between D_0 and $1/\chi$.

Results are available for diffusion in β -Ti¹⁹ but since the compressibility change of the solvent (titanium) is greater than that of the solute elements, see Fig. 4, it is unlikely that compressibility of the diffusing solute atom will be a major factor in determining Q . Data are also available for diffusion in chromium²⁰ but since two slopes are obtained for iron diffusion in chromium and since it is now known that chromium self diffusion is described by a single Q ,²¹ doubt is cast on the equation for iron diffusion in chromium. These data are therefore unusable. The only other bcc metal in this period is vanadium. Self-diffusion and the diffusion of iron have been measured in this element.²² The values of Q (V—74 kcal per mole; Fe—70 kcal per mole) and $1/\chi$ (V— 1.66×10^{-12} dyne per sq cm, Fe— 1.69×10^{-12} dyne per sq cm) are so similar that again it may be claimed that $1/\chi$ pre-

dicts the value of Q . The lack of other diffusion data in the metal preclude any firm conclusions regarding the importance of the compressibility of the diffusing atom. Tentatively, it may be said that compressibility predicts Q for impurity diffusion in iron to within ± 2 to 3 kcal per mole, (which may be a sufficiently accurate prediction in many cases), and possibly for diffusion in the other transitional metals.

Close agreement between tracer and probe analyzer results has been observed in the present work, Fig. 3; Eqs. [9] and [12]. This single result may be fortuitous at present, although the data of Hannemann *et al.*²³ on the analysis of incremental diffusion couples tend to confirm the similarity of the two techniques. Their result for an Fe-0.5 pct V alloy is

$$\tilde{D} = 0.6 \exp\left(-\frac{63,800}{RT}\right) \quad [24]$$

This is in excellent agreement with Eq. [10]. Their value, \tilde{D} , can be equated to the tracer diffusion coefficient D_v by

$$\tilde{D} = (N_v D_{Fe} + N_{Fe} D_v) \left(1 + \frac{d \ln \gamma_{Fe}}{d \ln N_{Fe}}\right)$$

for $N_{Fe} \gg N_v$ (e.g., Fe-0.5 pct V) $\ln \gamma_{Fe} \rightarrow 0$; $\tilde{D} = N_{Fe} D_v$ and therefore $\tilde{D} \approx D_v$. Agreement has also been observed between the tracer results of Rothman *et al.*²⁴ and the microprobe data of Speich *et al.*²⁵ for copper diffusion in iron.

Thus it would seem that compatibility between probe analysis and tracer results can be claimed provided that:

- i) incremental diffusion couples are used,^{23,25} or,
- ii) the same conditions are used as for tracer analysis (present work).

A further confirmation of this agreement has also been observed.¹ This compatibility between the two techniques can be of importance when no suitable isotopes are available for tracer studies.

The activation energy for impurity diffusion by a vacancy mechanism can be expressed as¹⁸

$$Q = \Delta H_m + \Delta H_f - C \quad [25]$$

where ΔH_m is the enthalpy of motion of a vacancy. (This is also made up of two other terms but these may be neglected; see Ref. 18, for a detailed discussion of Eq. [25].) ΔH_f is the enthalpy of formation of a vacancy, and

$$C = R \left[\frac{d \ln(fa^2 \nu_0)}{d \left(\frac{1}{T}\right)} \right]$$

where

f is a correlation factor (~ 0.7)

a is the lattice parameter, and

ν_0 is the Debye frequency ($\sim 10^{13}$ sec⁻¹).

C described the temperature dependence of f , a^2 , and ν_0 and can lead to nonlinearity in the Arrhenius plots. Its effect on the current Arrhenius equations was not measurable in terms of nonlinearity. Its value is therefore probably less than the experimental error of ~ 1 kcal per mole. Values of ΔH_m , ΔH_f , and particularly C (since it is so small) cannot be accurately

Table V. Values of Activation Energy, Positive and Negative Entropy Terms, and a Comparison of Calculated and Experimental Values of Entropy for Solute Diffusion in α - and γ -Fe

	Q	$(\Delta S)_{\text{exp}}$	$-\Delta S_0$	αQ	ΔS_{calc}
	kcal per mole	cal per mole, deg K ⁻¹			
Chromium in α -Fe	59.9	14.6	9.4	24.0	11.6
Vanadium in α -Fe	57.6	13.0	10.6	23.6	11.1
Hafnium in α -Fe	69.3	10.8	16.9	27.7	8.3
Chromium in γ -Fe	69.7	14.2	13.7	27.9	10.6
Vanadium in γ -Fe	63.1	6.9	18.3	25.2	7.6
Hafnium in γ -Fe	97.3	25.7	13.2	38.9	18.6

determined without information on impurity atom-vacancy interactions in transitional metals. No such information is available. Consequently, a meaningful discussion of these values is not possible at present.

A number of explanations can account for the slow diffusion of hafnium, e.g., i) a high enthalpy of motion, in view of its large atomic diameter, ii) a marked correlation of iron atom jumps. However, this is not likely to have a major effect as it has already been stated that correlation of jumps had no observable effect on the results, or iii) a hafnium atom-vacancy repulsion may occur. The most probable explanation is that slow diffusion rates are due to the hafnium atom having a low probability, due to its large size, in overcoming the energy barrier between adjacent lattice sites. Further study is required before a more conclusive answer can be stated. In the case of chromium and vanadium diffusion, values of Q are so near to the self diffusion activation energy that it is not possible to discuss them without more knowledge of the behavior of transitional atoms during atomic jumps.

Values for the entropy of diffusion may be derived from the equation¹⁸

$$\Delta S_{\text{exp}} = R \left[\frac{\ln D_0}{fa^2 \nu_0} \right]$$

and are given in Table V.

The entropy factor is made up of two terms,¹ one positive and the other negative,

$$(\Delta S)_{\text{exp}} = \Delta S_0 + \alpha Q$$

The negative term, ΔS_0 , is equated to $-\alpha Q - (\Delta S)_{\text{exp}}$. It may be determined using a value of 0.4×10^{-3} per deg for α , see Ref. 1. These results confirm the work of Dienes²⁶ who postulated that the entropy of diffusion is made up of a number of terms, one of which is negative. In the present work $\Delta S_0 \approx \frac{1}{2} \alpha Q$. For the anomalous metals, where the total entropy is small, Gibbs²⁷ has shown that ΔS_0 can exceed αQ , resulting in the low observed values of D_0 .²⁸ Theoretical values of ΔS may be determined from the equation²⁹

$$\Delta S_{\text{calc}} = 2Q\tau(\gamma - \frac{1}{3}) \quad [26]$$

where τ is the volume thermal expansion coefficient, and γ is Gruneisen's constant (2 for fcc and 3 for bcc metals). Theoretical and experimental values are compared in Table V.

Agreement is reasonable and although the difference is approximately 3 cal per mole per deg K in many instances, Eq. [26] will predict values of ΔS of the correct order of magnitude. Considering the rapidity with which D_0 can change (due to the exponen-

tial dependence of D on temperature) this method offers a reasonably accurate means of calculating D_0 in the absence of experimental data. Values of Q for Eq. [26] can be determined as in Fig. 4.

Entropy is also made up of the entropy of formation (ΔS_f) and motion (ΔS_m) of a vacancy. Again, accurate values cannot be calculated since impurity atom-vacancy interactions have not been determined.

The similarity between hafnium and other transitional metal diffusion (for the D_0 and Q values) for diffusion in α -Fe, but not in γ -Fe, would indicate that there is a critical space for hafnium atoms to move relatively freely which exists in α -Fe but not in γ -Fe.

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