

# A Commentary on: “Diffusion of Carbon in Austenite with a Discontinuity in Composition”\*

H.K.D.H. BHADESHIA

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CONSIDER an allotropic transition between two phases in a pure substance. The phases are said to be in equilibrium when they have identical free energies. Pure ice and water coexist at precisely 273.15 K (0 °C) and 1 atm of pressure. When this system consists of a mixture of common salt and H<sub>2</sub>O, the ice and water become solid and liquid solutions, respectively, but can still coexist in equilibrium, albeit under different circumstances. Yet, it has been known for many centuries that these impure phases have different chemical compositions, water being richer in salt than in ice. The astonishing fact is that there is no tendency for the salt to diffuse from the water into the ice to homogenize concentrations, no matter how long the mixture is observed. With solutions, it is not the free energy of the individual phases that must be equal for equilibrium to be achieved; rather the *chemical potentials* of the components (H<sub>2</sub>O and NaCl) must be uniform everywhere. This potential can be paraphrased as the mean free energy of a component in a solution of given composition. If all the potentials in the system are uniform, then there is no driving force for diffusion irrespective of spatial variations in concentration.

When attempting to validate his laws of diffusion, the physiologist Fick used water and salt to conduct experiments. The diffusion flux, he proposed, depends on the concentration gradient. However, at some stage, it was realized that it should depend on the negative gradient of the chemical potential. A flux driven in this manner would lead to a reduction in free energy, which after all, is what is required for any process to occur spontaneously. I am not sure when this realization came about, but Darken refers to an 1888 article by Nernst on osmotic pressure.

But the real motivation for Darken’s 1949 article was to demonstrate experimentally that “for a system of more than two components it is no longer necessarily true that a given element tends to diffuse towards a region of lower concentration.” The chemical potential gradient of that element may have a different sign to its

concentration gradient. When dealing with a single phase, the chemical potential gradient has the same sign as an activity gradient so that the latter sometimes is used in describing diffusion.

As pointed out by Darken, evidence for such diffusion could be found in a 1931 article by Hartley<sup>[1]</sup> on “the distribution of a molecular solute [acetone] in a solvent [water] containing a gradient of concentration of a second solute [salt].” But he wanted to demonstrate this in the solid state; it should be borne in mind that the nature of diffusion in solids was, at the time, the subject of much debate. Proof for the vacancy mechanism for substitutional diffusion only just had been presented by Simgelkas and Kirkendall<sup>[2]</sup> to an audience, which was not entirely receptive.

The samples that Darken fabricated were similar to those in earlier work in which dissimilar steels were joined together to study diffusion.<sup>[3,4]</sup> However, his goal was to realize the role of chemical potential gradients rather than to measure diffusion coefficients. Darken welded together two steels with similar carbon concentrations but different silicon concentrations. The choice of silicon as a substitutional solute seems to have been based on work by Smith, whose article<sup>[5]</sup> on the activity of carbon in ternary steels predates that of Darken but is referred to by him as unpublished work. Smith demonstrated experimentally that silicon dramatically increases the activity of carbon in austenite, more so than manganese. The composition of the silicon-rich side of the weld was such that the whole of the diffusion couple would be austenitic at the heat-treatment temperature. It was understood that substitutional solutes would diffuse at a rate that is much less than the interstitial carbon so the carbon could be considered to migrate within an essentially fixed distribution of silicon.

Darken succeeded in demonstrating the “uphill diffusion” of carbon and at the same time proved that although as a consequence of this diffusion, the carbon concentration changed discontinuously at the weld junction, the activity did not. He pointed out that Smoluchowski<sup>[2]</sup> did not observe a similar partitioning of carbon in a diffusion couple containing a discontinuity of cobalt concentration, implying that the influence of cobalt on the activity of carbon is small in comparison with that of silicon. We now know that this is, in fact, the case.<sup>[6]</sup>

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H.K.D.H. BHADESHIA, Professor, is with Materials Science and Metallurgy, University of Cambridge, Cambridge, UK. Contact e-mail: hkdb@cam.ac.uk

\*L.S. Darken, *Trans. AIME*, 1949, vol. 180, pp. 430–38.

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Darken's work has important technological consequences in the conversion of fossil fuel into electricity and, hence, widely is referred to in applied research. Superheated steam is used to turn large turbines that drive machines that convert mechanical into electrical energy. The turbines themselves are made of steel and have large temperature gradients along their length. This means that creep-resistant steel containing large chromium concentrations must be joined to tougher steel containing a reduced quantity of chromium, with similar carbon contents in both alloys. As a consequence, carbon is driven to migrate into the chromium-rich steel to establish a uniform chemical potential across the junction. A complication is that the partitioned carbon then combines with chromium to precipitate an intense zone of carbides in the vicinity of the weld junction, making the joint susceptible to failure.<sup>[7]</sup> This problem persists in modern power plants and also extends to joints between metals with different crystal structures. The theory for uphill diffusion with adaptations to account for multiple phases covers all these scenarios.

There is another interesting outcome for fundamental research. The idea that solute can be trapped by a moving interface achieved prominence when rapid solidification studies were at their most active in the early 1970s. A solute is said to be trapped when its chemical potential increases on transfer across the interface. The concept actually is a lot older than rapid solidification because this is exactly what happens to carbon during the martensitic transformation of steel.

The notion that the chemical potential increases goes against intuition, but this can happen in a multicomponent system in which the transfer of other species leads to an *overall* reduction of free energy despite the counterintuitive behavior of a particular solute. In other words, Darken's original statement quoted at the beginning of this note could be generalized to read the following: for a system of more than two components, it is no longer necessarily true that a given element tends to diffuse toward a region of lower chemical potential.

Would Darken have thought of these experiments were it not for the passionate discussion ("skepticism") that followed his earlier work on binary diffusion?<sup>[8,9]</sup> And given the huge discrepancy in the diffusion rates of carbon and substitutional solutes, I wonder whether the result would have been so vivid had he chosen a system other than steel.

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# Diffusion of Carbon in Austenite with a Discontinuity in Composition

BY L. S. DARKEN,\* MEMBER AIME

† (Philadelphia Meeting October, 1948)

It has long been recognized that the driving force in an isothermal diffusion process may be regarded as the negative gradient of the chemical potential (partial molal free energy) of the diffusing substance. This equivalence is exactly analogous to the fact that a mechanical force is the negative gradient of the potential energy. Nernst<sup>1</sup> in 1888 expressed these driving forces in terms of osmotic pressure, which is directly related to the chemical potential and free energy.

The relationship between the diffusivity, mobility and activity coefficient of electrolytes in aqueous solution has been developed in great detail by Onsager and Fuoss<sup>2</sup> with results which have recently been confirmed experimentally by Harned and Nuttall.<sup>3</sup>

This interpretation of the driving force in isothermal diffusion has been discussed earlier by the author,<sup>4,5</sup> who pointed out<sup>4</sup> that "for a system of more than two components it is no longer necessarily true that a given element tends to diffuse toward a region of lower concentration even within a single phase region"; departure from the behavior of an ideal solution may be so great that the concentration gradient and the chemical potential gradient, or activity gradient, may be of different sign, thus giving rise to "up hill" diffusion. Since, in the discussion of that paper,<sup>4</sup> some skepti-

cism as to the validity of this conclusion was expressed, it seemed desirable to adduce experimental evidence to support it.

Evidence of such diffusion in nonmetallic systems has already been reported. For example, it was observed by Hartley<sup>11</sup> in a series of experiments in which sodium chloride diffused from a saturated solution in about 5 pct acetone in water into a solution virtually free of salt but with essentially the same acetone concentration. Specifically, a wine glass containing crystalline salt and saturated solution was totally immersed in a large glass cylinder containing the acetone-water solution without salt; the difference in specific gravity was such as to prevent convection. Diffusion of salt was accompanied by a marked depletion of acetone in the wine glass; after 3 days the acetone concentration decreased from 5.37 pct at the top of the glass, where the salt concentration was low (0.93 pct), to 1.84 pct at the bottom where the salt concentration was high (21.64 pct). This "uphill" diffusion was found to be such that the partial pressure (activity) of acetone was essentially equalized throughout the system when a steady state gradient of sodium chloride was maintained.

In order to demonstrate the existence of such diffusion in metals, a series of four weld-diffusion experiments was made. In these measurements pairs of steel of virtually the same carbon content, but differing markedly in alloy content, were welded at the end and held at 1050°C for about two weeks. Subsequent analysis showed that carbon had diffused so as to produce an inequality

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\* Research Laboratory, United States Steel Corporation, Kearny, N. J.

<sup>1</sup> References are at the end of the paper.

of carbon content on the two sides of the weld.

#### EXPERIMENTAL

The specimens to be welded were rods 2½-in. long and ⅜, ½ or ⅝ in. in diam, ground flat at one end. Welds were made in an apparatus, patterned after that used by Wells and Mehl,<sup>6</sup> in which the rods were held in an adapter so that the ground surfaces met squarely. A helium atmosphere was used. A current of about 4500 amp was then passed through the rods;\* the temperature of the weld was measured by means of an optical pyrometer sighted through a mica window. When the observed temperature reached about 1125°C, which required 10 to 20 sec, the current was discontinued. All specimens were ground, polished and etched on the cylindrical surface and were then mounted on a jeweller's lathe and examined microscopically. All welds appeared sound with very few holes; the zone of fusion extended about 0.002 in. The departure of the welded zone from normality to the axis of the welded specimen was less than this amount. The position of the weld was marked with a center punch.

The original composition of the steels used is given in Table 1. Four welds were made as shown in Table 2.

The furnace in which the welded rods were heated so that diffusion could occur was of the vertically-mounted tubular type (18 in. long, 1½ in. bore), specially wound in three sections so that the relative current through each section could be adjusted to give a long central zone of temperature uniformity. After careful adjustment there was a central zone of nearly 6 in. over which the temperature variation was less than 1°C. The temperature was controlled by means of a commercial controller of 10 mv range, the major

\* The author wishes to express his thanks to Mr. J. F. Schmidt of Federal Shipbuilding and Dry Dock Co. for his assistance in providing equipment and supervising the delivery of this current.

TABLE 1—Composition of Steels Used

Designation	Per Cent C	Per Cent Mn	Per Cent Si	Per Cent P	Per Cent S	Per Cent Cr	Per Cent Mo
a	0.49	0.25	3.80	0.011	0.006	0.31	
b	0.04	0.28	4.78	0.006	0.011		
c	0.45	0.88	0.05	0.020	0.008		
d	0.58	6.45	0.14	0.035	0.008		
e	1.19	0.28	0.20				0.02
f	1.34	0.20	0.07				6.07

TABLE 2—Data on Welds

Weld Number	Steels Welded	Diameter (In.)	Time of Diffusion, Seconds	Temperature during Diffusion
1	a - b	⅜	1.210 × 10 <sup>6</sup>	1050°C
2	a - c	½	1.109	
3	a - d	⅝	0.821	
4	e -	⅝	1.210	

part of the emf of the chromel-alumel control couple being balanced by an independent potentiometer circuit; this arrangement reduced the temperature fluctuation during the control cycle to one or two tenths of a degree centigrade. The control couple was contained inside a silica well immediately adjacent to the center of the specimen. The calibration of the control couple was checked *in situ* at the beginning and end of each experiment by a master couple which had been compared with one certified by the Bureau of Standards. All specimens are believed to have been held within 1°C of the nominal temperature (1050°C) for the diffusion period.

The gas atmosphere used in the diffusion furnace was helium. Some preliminary difficulties were experienced in purifying this gas sufficiently that the constant slow flow would be essentially neutral to the specimens over the extended periods required. Finally an all glass train was used in which the gas (from a commercial cylinder) was first passed over oxidized copper (copper plus cuprous oxide) at 600°C to convert hydrogen and hydrocarbons to water and carbon dioxide; these were absorbed by passage over ascarite and phosphorous pentoxide; the gas was then

passed over reduced copper gauze at  $500^{\circ}\text{C}$  to remove traces of oxygen. The gas thus purified entered through a mercury seal into the bottom of the furnace tube proper

carbon distribution after diffusion is shown graphically in Fig 1, 2, 3, 4. The carbon content of the region beyond that shown graphically was uniform and is indicated

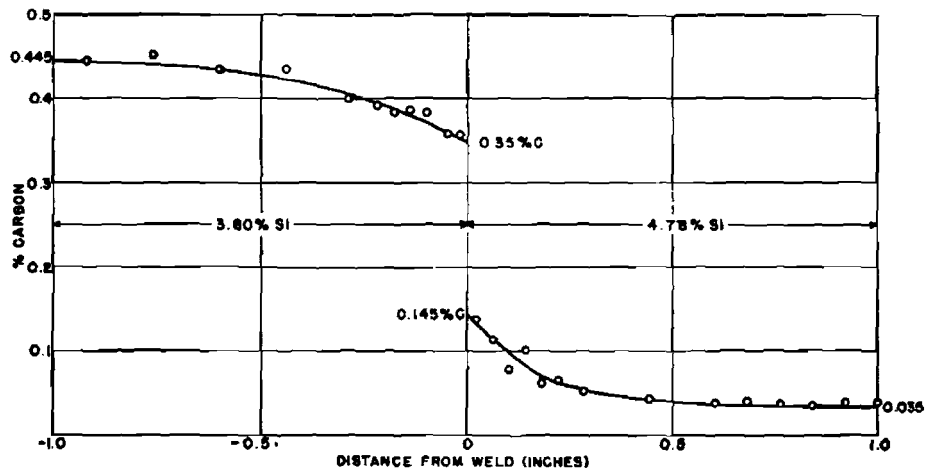


FIG 1—CARBON DISTRIBUTION IN WELDED SPECIMEN NO. 1 AFTER 14 DAYS AT  $1050^{\circ}\text{C}$ .

which was of 27 pct chrome steel. The specimens, suspended by a molybdenum wire, were prevented from making contact with the furnace tube by porcelain rings on each end. The effectiveness of the purification is attested by the fact that in no experiment except the first did the carbon content of the ends of the specimen (beyond the diffusion zone) change by more than 0.02 pct C.

After treatment of 10 to 14 days at  $1050^{\circ}\text{C}$ , the specimens were allowed to cool with the furnace to  $800^{\circ}\text{C}$ , which required about 20 min., and were then lifted into the head. This treatment was given instead of a quench in order to make the samples more easily machinable. On removal from the furnace the specimens were bright in appearance.

Samples for analysis were turned off on a precision lathe. The original center mark was used as reference for all measurements. The first six samples from the center were each 0.04 in. long and subsequent ones 0.08 in. This gave samples of about one half or one gram respectively, the whole of which was used for carbon analysis by the combustion method. The

numerically in the figures; these carbon contents are the average of four or more analyses.

#### “UPHILL” DIFFUSION OF CARBON

In the first specimen, steel *b* (to the right, Fig 1), was originally ferritic (even at  $1050^{\circ}\text{C}$ ) but considerable austenite formed in the diffusion zone on account of the rise in carbon content. In the fourth specimen, steel *f* (to the right Fig 4), contained carbide in addition to austenite. The remaining six of the total eight halves were completely austenitic during the diffusion period as determined by reference to phase diagrams, particularly those recently published by R. P. Smith.<sup>7</sup>

The “uphill” diffusion of carbon is most clear in the second and third welds (Fig 2 and 3). From Fig 2 it is seen that carbon diffuses from an austenite of carbon content 0.32 pct to an austenite of carbon content 0.59 pct. The difference in silicon content (3.89 and 0.05 pct respectively) is clearly responsible for this phenomenon. In the third weld, “uphill” diffusion is even more pronounced; in this case the carbon diffused from an austenite of 0.32 pct

carbon to an austenite of 0.72 pct carbon. The large difference is occasioned by the high silicon content of one side (3.89 pct)

two effects combine to give a pronounced migration of carbon to the high carbon side. In the fourth weld a similar effect is

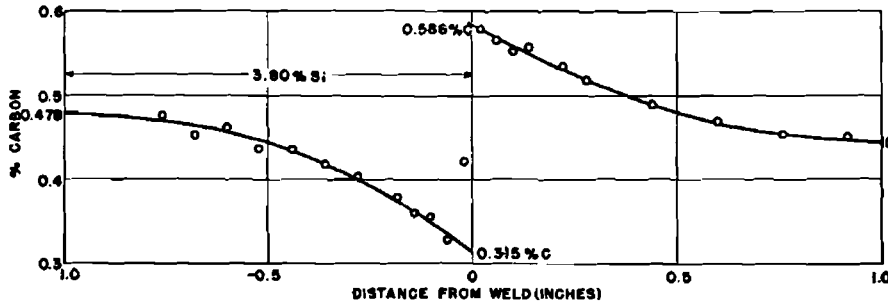


FIG 2—CARBON DISTRIBUTION IN WELDED SPECIMEN NO. 2 AFTER 13 DAYS AT 1050°C.

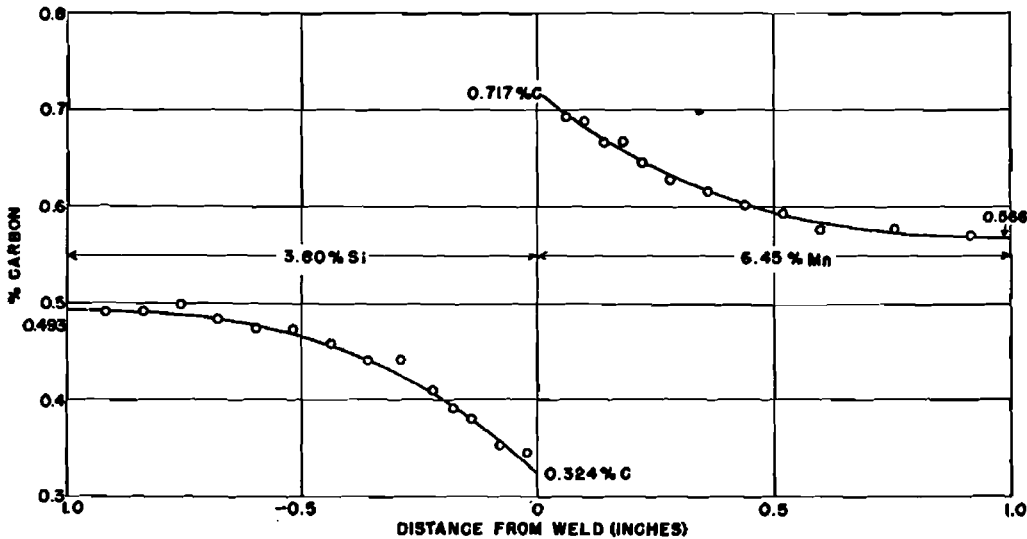


FIG 3—CARBON DISTRIBUTION IN WELDED SPECIMEN NO. 3 AFTER 10 DAYS AT 1050°C.

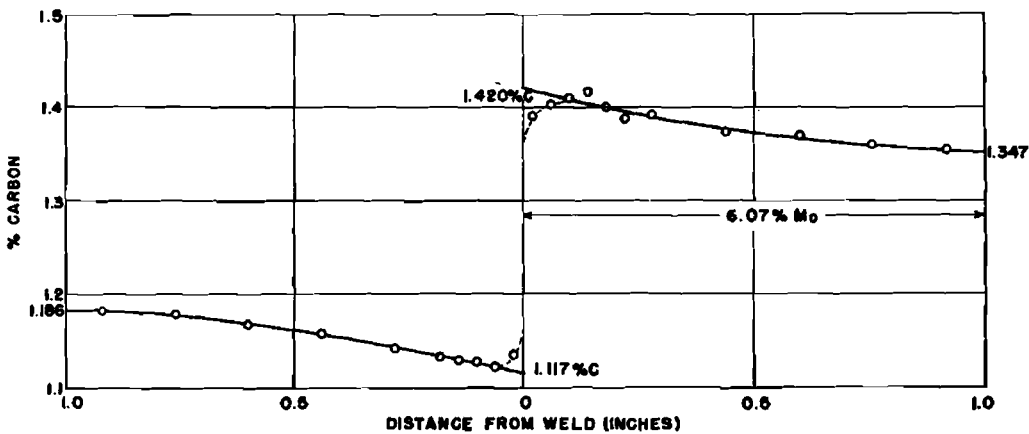


FIG 4—CARBON DISTRIBUTION IN WELDED SPECIMEN NO. 4 AFTER 14 DAYS AT 1050°C.

and the high manganese content (6.45 pct) of the other. Thus, silicon decreases and manganese increases the affinity of austenite for carbon. In the third weld these

observed; the carbon diffused from austenite containing 1.12 pct carbon into steel containing 1.42 pct carbon and 6 pct molybdenum. However, as mentioned

previously, this composition lies in the field of austenite plus carbide; the composition of the austenite is believed to be about 1.26 pct carbon and 2 pct molybdenum. It may, on this basis, be tentatively concluded that molybdenum increases the affinity of austenite for carbon to a somewhat greater extent (for equal weight percent) than does manganese.

Smoluchowski<sup>8</sup> performed some similar experiments wherein iron-cobalt-carbon alloys were welded to iron-carbon alloys. These welds were held at 1000°C for several days for diffusion to occur. Subsequent analysis disclosed no discontinuities in carbon content at the weld. He also performed a separate experiment to prove this; a sample with 4 pct cobalt and another without cobalt, both containing 0.80 pct carbon, were welded and kept together for several days at 1000°C but no change in the carbon distribution was detected. The absence of such effect in cobalt alloys is in marked contrast to the pronounced effect of silicon, manganese and molybdenum; it should be noted, however, that these latter elements were chosen because it was expected that they would have a relatively large effect.

Although there is a discontinuity (or near discontinuity) in carbon concentration at the weld, in the derivation of the diffusivity from the chemical potential<sup>6,9</sup> the equality of chemical potential or activity at zero distance on either side of the weld is tacitly assumed: that is, the rate of diffusion is taken proportional to the gradient of the chemical potential times the mobility times the concentration. As a

finite rate is observed, the gradient of the chemical potential must be finite at all points provided the mobility and concentration are also finite; therefore the chemical potential must be single valued at all points and cannot suffer a discontinuity. For this reason it is of interest to compare the activity of carbon immediately adjacent to the original weld on both sides. At the compositions of each side (at zero distance) the activity of carbon was obtained from the data of R. P. Smith<sup>7</sup> for the second and third welds. The slight difference in temperature (50°C) is regarded as insignificant. The agreement is seen to be within the experimental error. (In the table no correction was made for the effect of 0.3 pct Cr on the activity of carbon in the high silicon steel; it is believed that such correction would be about -0.01 thus making the agreement even better.)

There is of course no strict discontinuity in the concentration of silicon or manganese at the position of the original weld (Fig 1, 2, 3, 4) as there is some slight diffusion of these elements as well as of carbon. On this account, the percentage of carbon also does not change abruptly at the weld but merely very rapidly in this vicinity; slight evidence of this may be seen in Fig 4. The interpretation of this effect is aided by recalling that at all times composition-distance curves as in Fig 1, 2, 3 or 4 are similar; for example, if the specimen of Fig 2 had been held at temperature four times

TABLE 3—Comparison of Activity of Carbon on the Two Sides of the Welds

Weld No.	Left Side (Fig 2, 3)				Right Side			
	Per Cent C	Per Cent Si	Per Cent Mn	Activity of Carbon	Per Cent C	Per Cent Si	Per Cent Mn	Activity of Carbon
2	0.31 <sub>5</sub>	3.80	0.25	0.30	0.58 <sub>8</sub>	0.05	0.88	0.29
3	0.32 <sub>4</sub>	3.80	0.25	0.31	0.71 <sub>7</sub>	0.14	6.45	0.29

as long the composition-distance curve would be the same as though Fig 2 were stretched to  $\sqrt{4} = 2$  times its present length provided the specimen were very

silicon at increasing time intervals is shown. Thus it is seen that eventually the specimen does tend to approach the true equilibrium state of uniform composition;

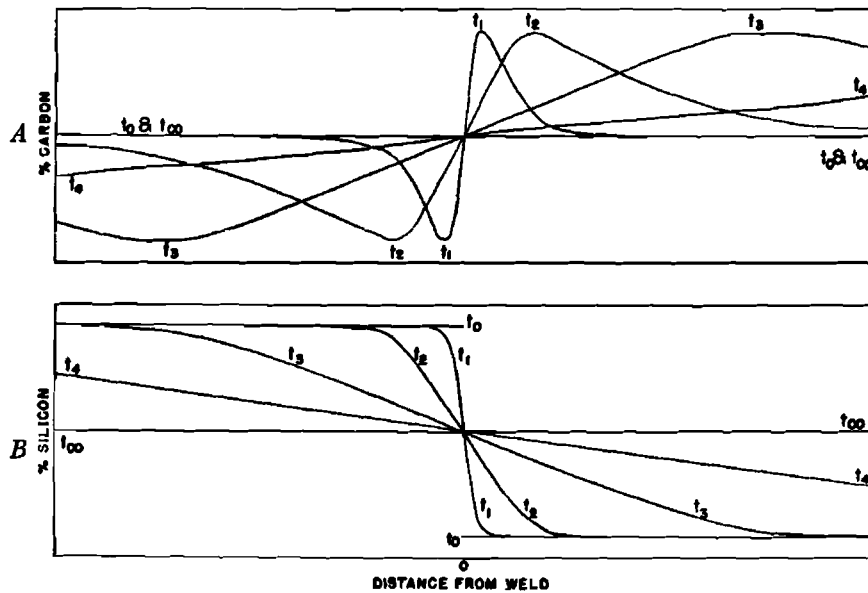


FIG 5—SCHEMATIC DIAGRAM SHOWING THE CHANGE WITH TIME OF CARBON DISTRIBUTION *A* AND SILICON DISTRIBUTION *B* FOR A WELDED SPECIMEN BOTH HALVES OF WHICH WERE INITIALLY OF THE SAME CARBON CONTENT BUT OF DIFFERENT SILICON CONTENT.

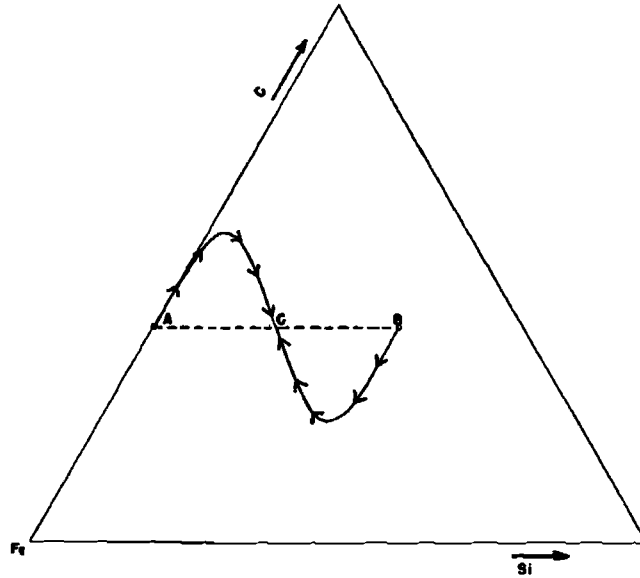


FIG 6—SCHEMATIC DIAGRAM SHOWING THE CHANGE IN COMPOSITION OF TWO POINTS ON OPPOSITE SIDES OF THE WELD IN ULTIMATELY APPROACHING UNIFORMITY OF COMPOSITION.

long. Thus at longer times the lack of discontinuity would become more evident and composition curves would be similar to those shown schematically in Fig 5A and 5B in which the distribution of carbon and

however, the method of approach to equilibrium is hardly the shortest. This is shown schematically in Fig 6. Here *A* and *B* represent the initial composition of the two steels. Considering two points in the



specimen at equal distance but on opposite sides of the weld, the change of composition of each as time progresses is shown by the two parts of the full curve which both approach, at very long times, the common point C. Although the system eventually approaches the point of lowest free energy the path taken departs considerably from the direct one shown by the dotted line. The reason for this is clearly that the diffusivity of carbon is so much greater than that of silicon.

#### DETERMINATION OF DIFFUSIVITIES

Although determination of numerical values of the diffusivity was not the primary purpose of this investigation, nevertheless, the data readily lend themselves to such purpose since each half of each specimen may be regarded as a semi-infinite solid, initially of uniform composition, the boundary of which was maintained at essentially constant composition for the duration of the diffusion period. The range of carbon content was sufficiently small that the diffusivity of carbon may be regarded as constant. The solution of the diffusion equation for this case is well known and given by the following equation:

$$\frac{C - C_0}{C_\infty - C_0} = \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda \\ \equiv \varphi \left( \frac{x}{2\sqrt{Dt}} \right)$$

where C = per cent carbon at  $x$  and  $t$   
 $C_0$  = per cent carbon at interface  
 $C_\infty$  = per cent carbon at great distance from the interface  
 $x$  = distance from interface  
 $t$  = time of diffusion  
 $D$  = diffusivity (of carbon)  
 $\lambda$  = integration variable  
 $\varphi$  = probability integral

In the author's opinion the two best methods of obtaining a numerical value of

the diffusivity from the data and this equation are as follows:

Method 1: From the preceding equation it follows immediately that  $\frac{x}{2\sqrt{Dt}}$  is the inverse probability function of  $\frac{C - C_0}{C_\infty - C_0}$ . Therefore a plot of the inverse probability function of  $\frac{C - C_0}{C_\infty - C_0}$  vs.  $x$  should pass through the origin and have a slope equal to  $\frac{1}{2\sqrt{Dt}}$ . Such plots were made for all the half specimens which were entirely austenitic and  $D$  was evaluated with results shown in Table 4.

Method 2: The foregoing equation may be rearranged, multiplied through by  $dx$  and integrated (at constant  $t$ ) with the following result.<sup>4</sup>

$$\int_0^\infty (C_\infty - C) dx \\ = 2(C_\infty - C_0) \sqrt{Dt} \int_0^\infty \int_\lambda^\infty e^{-\lambda^2} d\lambda$$

As the definite double integral has the value  $1/\sqrt{\pi}$  it follows that

$$\int_0^\infty (C_\infty - C) dx = 1.128(C_\infty - C_0) \sqrt{Dt}$$

The integral on the left is equal to the amount of carbon which has crossed the interface and was evaluated from the experimental data by integration of the curves (Fig 1-4) with the aid of Simpson's rule.\* Diffusivities thus evaluated with the aid of the immediately foregoing equations are also shown in Table 4.

The diffusivity of the two plain carbon steels as calculated from the equation given by Wells and Mehl as representing their results is also shown in Table 4. The agreement is within the experimental error,

\* This integration also affords a check on the experimental error since the carbon which leaves one side enters the other (except for

although the present data would tend to indicate a slightly smaller effect of carbon content on the diffusivity than that reported by them.

Smith<sup>7</sup> on the activity of carbon in iron-silicon alloys permit a comparison of the above observed effect of silicon on the diffusivity of carbon with that predicted

TABLE 4—Diffusivity of Carbon in Austenite at 1050°C

Steel	Weld	Mean Per Cent C	Diffusivity, $\frac{\text{cm}^2}{\text{sec}}$			
			Method 1	Method 2	Average (This Research)	From Equation of Wells and Mehl
a	1	0.4 <sup>0</sup>	$3.9 \times 10^{-7}$	$3.4 \times 10^{-7}$	$3.9^* \times 10^{-7}$	
	2	0.4 <sup>0</sup>	4.0	4.0		
	3	0.4 <sup>0</sup>	4.1	4.2		
c	2	0.5 <sup>1</sup>	5.9	5.5	5.7	$5.3 \times 10^{-7}$ (6)
d	3	0.6 <sub>4</sub>	5.7	5.2	5.4	
e	4	1.1 <sub>8</sub>	6.9	6.5	6.7	

\* If the less reliable results from the first specimen are omitted the average is  $4.1 \times 10^{-7}$ .

The diffusivity found for steel *c* is also in agreement with the observation of Wells and Mehl that the effect of manganese on the diffusivity is small, interpolation of their data (between 0 and 16 pct Mn) yields a diffusivity of about  $6 \times 10^{-7}$  as shown parenthetically in Table 4. The effect of silicon in decreasing the diffusivity seems quite definite as all experiments with steel *a* yield a diffusivity appreciably lower than that found for plain carbon steels of the same carbon content (at this carbon content the diffusivity of a plain carbon steel is 5.0 or  $5.5 \times 10^{-7}$  as determined from Wells' and Mehl's or the present data.

The recent accurate measurements of

loss from the specimen); thus for the two halves of a welded specimen the integral  $\int_0^\infty (C_\infty - C) dx$  should be equal (except for sign). That this is essentially so is shown by the following table of values of the integral in pct C  $\times$  inches

$$\int_0^\infty (C_\infty - C) dx$$

WELD NO.	LEFT SIDE	RIGHT SIDE
1	+0.027	-(0.018)
2	+0.048	- 0.050
3	+0.043	- 0.046
4	+0.027	- 0.028

The agreement is good for all specimens except the first. The discrepancy in this case may be caused by the high diffusivity of carbon in ferrite which would give rise to a long tail on the curve of Fig 1. The tabulated area does not include any such tail.

by Eq 12 of Birchenall and Mehl.<sup>10</sup> This equation may be rewritten

$$D = D_1 \gamma \left( 1 + C \frac{d \ln \gamma}{dC} \right)$$

where  $D_1$  is regarded as constant;  $\gamma$  is the activity coefficient of carbon in austenite;  $C$  is carbon concentration. The data of Smith indicate that the terms in parenthesis change little, if any, as the silicon content of austenite is increased. However, he found that  $\gamma$  increased by a factor of approximately two as the silicon content increased from zero to 4 pct. Hence, on the basis of the foregoing equation the diffusivity of carbon would be expected to be about twice as great in steel *a* as in steel *c*; as the observed value of the diffusivity is appreciably smaller for steel *a* than *c*, the validity of their equation seems to be in serious question. The theoretical basis for such doubt has been discussed by the author elsewhere.<sup>5</sup> It might be added that a similar comparison of manganese steels with plain carbon steels shows a discrepancy between the observed increase of carbon diffusivity occasioned by 16 pct manganese (about 30 pct at 1 pct C) with that calculated from Birchenall and Mehl's equation with the aid of Smith's data (about 80 pct at 1 pct C).

## SUMMARY

After welding two alloy steels together and then permitting diffusion by holding the specimen at 1050°C for about two weeks, concentration-penetration curves of carbon were determined by analysis. Four such experiments were performed. In two of the specimens, which were wholly austenitic during the diffusion period, it was found that carbon diffused from the low carbon side to the high carbon side. At approximately equal carbon contents carbon diffuses from a high-silicon to a low-silicon austenite and from a low-manganese to a high-manganese austenite. This effect is quantitatively explained by reference to recent data on the activity of carbon in iron-silicon and iron-manganese alloys. The activity of carbon, relative to graphite, is identical on both sides of the weld (immediately adjacent thereto). In the immediate vicinity of the weld the steel itself acts as a semipermeable diaphragm, permeable to carbon but relatively impermeable to silicon and manganese by virtue of the much smaller diffusivity of these latter elements of austenite. Thus the activity of carbon is equalized on the two sides of the weld

independent of the near discontinuity in the activity of manganese or silicon.

From the same data, the diffusivity of carbon in the several austenites at 1050°C was determined. For comparable compositions, the results are in good agreement with those of Wells and Mehl. Silicon decreases the diffusivity of carbon in austenite, whereas equilibrium measurements show that silicon markedly increases the activity coefficient of carbon in austenite.

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