Diffusion in metals: the flux of history

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It is 150 years since the first equation was proposed for the rate of flow of a constituent by diffusion. Alternative equations have been proposed over the years for this basic, underlying flux, i.e. excluding the various complications that vie to bog down the subject. A brief commentary is offered on the alternative equations available for this Fick's first law of diffusion, and their consequences for the time dependency of local concentration (Fick's second law) and chemical interdiffusion of a mutual solution. It is suggested that, while the preferred choice for the flux equation is rather more debatable than is commonly assumed, the actual differences between the rival formulations might be rather less than would be expected.

Keywords: Solute diffusion, Flux equation, Metals

Introduction

Adolf Fick proposed his famous flux equation in 1855,[1] whereby the diffusive flux J of atoms is proportional to the concentration gradient dC/dx, with the coefficient of proportionality being the diffusion coefficient D

$$J = -D\,\frac{\partial C}{\partial x} \tag{1}$$

Originally, D was considered constant (at temperature) and thus was taken outside the differential.[2] This was an intelligent guess, copying the format of Fourier's heat flux equation. This can be viewed either 'macroscopically' as the steady state solution across a sample with fixed concentrations on either side, or 'microscopically' as the current, local flux at a particular place and time. Any imbalance in the local fluxes around a particular point necessarily lead to changes in that local concentration with time, according to Fick's second law, i.e. for unsteady state diffusion (see Appendix). As Darken and Gurry put it: 'what goes in and does not go out, stays there.' (p. 438)[2]

$$\frac{\partial C}{\partial t} = D\cdot\,\frac{\partial^2 C}{\partial x^2} \tag{2}$$

The present discourse concentrates on the ensuing variants of this basic flux equation for solid state diffusion: for a general historical review of the development of the subject, the reader is referred to Tuijn.[3] Fick's 'laws' proved successful in various areas but with the arrival of techniques capable of measuring concentration gradients in solids, it became evident that the data usually diverged from these predictions: concentration was influencing diffusion over and above the direct effect of the concentration gradient even in simple, isotropic systems such as typical metals. Highly concentrated solutions are necessarily not 'simple' concerning descriptions of diffusion, but apparent effects of concentration were being noticed at fairly mild concentrations. It was clear that a modified formulation was required to predict at least a first approximation of how concentration affected diffusivity. The accepted formulation was to make the diffusion coefficient an unknown function of concentration D_C. However, rather than considering it equally as variable as the concentration and including it within the differential term, it was deployed as a coefficient multiplying the concentration gradient in the first law, and only included within the differential term for the generation of Fick's second law from this

$$J = -D_C\,\frac{\partial C}{\partial x} \tag{3a}$$

$$\therefore\ \frac{\partial C}{\partial t} = \frac{\partial(D_C\cdot\partial C/\partial x)}{\partial x} \tag{3b}$$

There is no real dispute about the generation of the second law from the first, but the nature of D_C and the first law, i.e. the underlying flux equation, have proved surprisingly controversial.

One further standard equation will be presented here as a reminder to the reader, with all further equations, concerning the arguments, confined to the appendix. The equations so far are akin to the original analogy of heat flux, where the material merely serves as a medium to house this flux. In solute diffusion, particularly regarding substitutional elements, the medium itself takes part in the diffusion process. The accepted, overall diffusivity was devised from those of the component elements. The flux equation (here in relation to the equal flux Boltzmann–Matano interface) for a simple binary system of substitutional components A and B with an equilibrium concentration of vacancies becomes[4]

$$J^{AB} = -(C_A D_B + C_B D_A)\cdot\,\frac{dC_A}{dx} \tag{4}$$

The controversy referred to in relation to equation (3)

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concerning the nature of D_C applies likewise to the diffusivities of the components A and B in equation (4).

An account of the development of these standard and the alternative forms will now be presented.

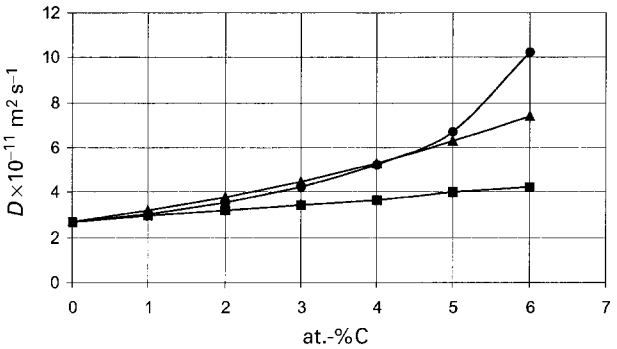
Activity and thermodynamic factor

In 1942, Darken proposed that diffusion might depend on the gradient of the 'effective' concentration, i.e. of the activity, rather than of the actual concentration *per se*.[5] Thus started a long and sometimes acrimonious debate that appears to have been swept under the carpet rather than ever actually settled. His suggestion was essentially just intuitive, and it did not go down well. The attack in the recorded discussion was led by Professor Mehl: 'There is no necessary relation between thermodynamic quantities and kinetic or rate phenomena.' However, by 1947, Mehl had changed his mind and, with Birchenall,[6] supported this activity gradient formalism, citing experimental evidence from the then best available data for systems with known thermodynamic and diffusion data as required to test the proposition. These were Cu–Zn brass (substitutional) and Fe–C steel (interstitial). In an intriguing reversal of roles, Darken was vociferous in counterattack, 'I would not expect a general relation between mobility (characteristic of rate) and activity coefficient (characteristic of equilibrium).'[6] Perhaps he enjoyed the irony, but his counterargument was itself thermodynamic. He saw the free energy gradient as being the key. The following year, Darken expounded this view,[7] proposing his now standard 'thermodynamic factor', θ (see Appendix), that would adjust the value for the diffusion coefficient relevant to the case of infinite dilution D_0 to the case of a finite solute concentration D_C. He remarked that similar arguments were already in existence outside of their metallurgical remit, notably due to Onsager.[8] As before, he was given a 'hard time' for his theoretical ponderings, again notably by Mehl: 'It is obvious that the solution to this problem is to be found in the laboratory and not at the desk'.[7] He was criticised for assigning more importance to his thermodynamic, phenomenological approach than to any consideration of mechanism. Darken's assailants looked forward to the following paper, by Hollomon, for a *proper* assessment of diffusion. But Hollomon then rescued him from the onslaught in the recorded discussion, seeing it as an excellent paper.

Hollomon's following paper, coauthored with Fisher and Turnbull,[9] considered diffusion in the manner of a chemical reaction, with the highest energy configuration of the atom jump, i.e. at the 'saddle point', being akin to the activated complex controlling the rate of a chemical reaction. Simplification of the resultant equation required an assumption to be made regarding the activity coefficient of this 'activated complex'. Notably, the flux was proportional to the ratio of the activity coefficients γ in the adjoining lattice sites, to that of the activated complex. If they were assumed to be proportional to each other, they cancelled out barring a numerical constant and one obtained Darken's equation. If it was assumed that the saddle point had its own, constant value of γ, independent of that in adjoining, proper lattice sites, the γ of the adjacent lattice remained, and Darken's thermodynamic factor would therefore also be multiplied by this γ. (For simplicity, the activities used here have the reference state of infinite dilution rather than of ideal solution, thereby γ tends to unity as C tends to zero and D tends to D_0.) They also pointed out that this latter result is mathematically identical to employing the activity gradient formalism of Birchenall and Mehl. Indeed, from the recorded discussion, it appears that the activity gradient formalism had come close to being regarded as standard theory at this stage. Darken (discussion of Ref. 6) argued that his Onsager style mobility term is best left without this extra γ factor as standard, leaving the residual variability to be fitted empirically. Curiously, instead, not only was this factor left off as standard, but it appeared to grow in status to the extent that woe betide anyone who dared add this or any other factor to it.

Darken also proposed the chemical interdiffusion equation for mutual solution (equation (4)) with the component Ds varying with concentration (to a first approximation) according to his thermodynamic factor, as above.[7] (This, and the version of equation (4) resulting from the 'extra γ' formulation, are included in the Appendix.) This presumed the vacancy mechanism, however, that had still not been generally accepted. The argument over the wayward γ factor became unduly tied up in arguments between him and Mehl over whether the underlying mechanism was by vacancy (Darken) or direct exchange (Mehl). Maybe that is the *de facto*, though inappropriate, reason for the activity gradient formalism losing the battle! Guy joined the fray, on the side of the activity gradient camp, in 1949[10] and Darken, who had proposed it only a few years before, was vehement in his attack: 'a pure postulate'; 'I do not believe the postulate has even an approximate general validity.' However, in the same recorded discussion, Wells and Batz conceded that it did fit their iron–carbon data rather well except at the highest values. They had recently published very extensive results for the diffusivity of carbon in austenitic iron over a wide range of concentration and temperature,[11] using the Matano–Boltzmann analysis to derive the values of D_C from non-steady state profiles. Smith was independently determining iron–carbon diffusivity data[12] by the alternative, steady state method, whereby different, constant concentrations were maintained across a specimen during isothermal treatment until the concentration profile between them stabilised, i.e. with a constant flux maintained thereafter through the specimen. He obtained gratifyingly good agreement with the data of Wells and Batz, and in 1950, likewise pointed out that the activity gradient formalism (which equates to Darken's thermodynamic factor but with an extra activity factor, see Appendix) was far superior to Darken's thermodynamic factor alone. An experimental comparison against Wells and Batz's data[11] is presented in Fig. 1,[13] with the predictions being fully consistent with those made by Smith at the time against his own data.[12] With either source for the experimental data, excellent agreement is obtained with the simple 'extra γ' formulation right up to 5 at.-% ($\sim$1·1 wt-%) before having to include the various complications associated with concentrated solutions.

LeClaire accepted carbon in iron as a clear case in point but went as far as to say that the activity gradient formalism may be sufficient for all simple systems.[14]

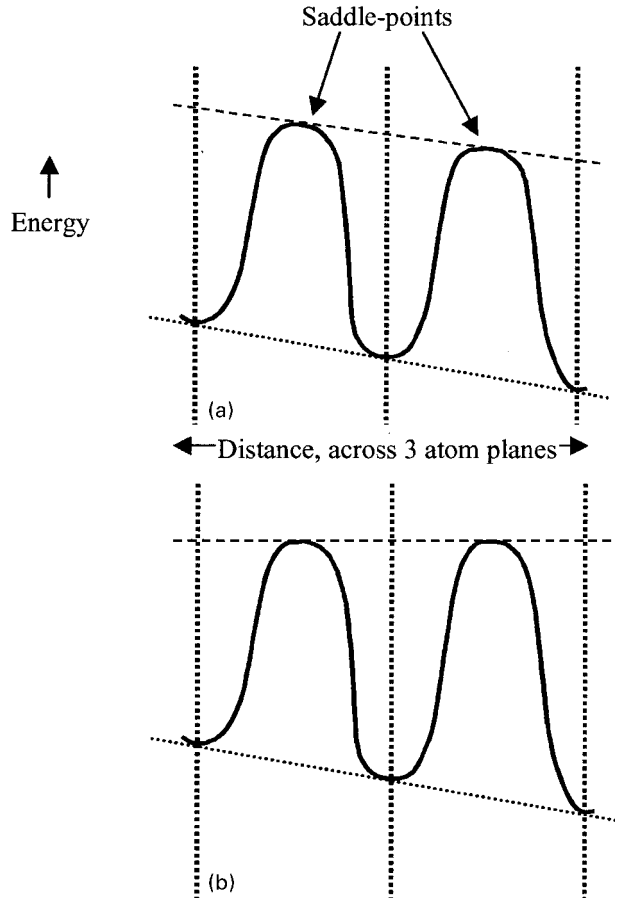


● experimental data[11]; Δ predictions from activity formulation[13]; ■ predictions from traditional formulation

1 The effect of carbon concentration on its diffusivity in fcc-iron at 1000°C[13]

However, to cover the general case, he suggested that one stayed with the simple Fick formalism and made the diffusion coefficient an arbitrary function of concentration that fitted the data. Darken did not assume that his thermodynamic factor covered all the concentration dependence, and that an empirically fitted mobility term was likely to be required (though in that case it would be tempting to follow LeClaire and simply fit a single, overall diffusion coefficient empirically without incorporation of the thermodynamic factor).

The battle, however, appeared to be lost. In 1955, Mehl appeared rather contrite,[15] conceding the vacancy mechanism, and employing Darken's analysis for interpreting the diffusivities within brass. The thermodynamic factor by no means accounted for all the concentration dependence, but that was quoted as the observed, empirical dependence of the underlying mobilities without even attempting to see if the activity coefficients helped to explain the discrepancy. Back in 1942 (discussion in Ref. 5) Darken had pointed out that the activity gradient formalism fitted the existing data for brass very well, quoting the example of a predicted increase in diffusion coefficient from zero to 20%Zn in alpha brass by a factor of over 7 (7·3 in fact, determined from his quoted equation for the activity of $\boldsymbol{a}=C\exp(0{\cdot}06C)$). In Mehl's new data of 1955, the observed increase over that range was a factor of around 8, whereas that predicted by the thermodynamic factor θ alone was only a factor of 2·2. No mention of this was made in the paper. Instead, the remaining variability after reduction by the thermodynamic factor was described as how the underlying mobility varies with concentration, and was left as empirical observation. In the same year, Resnick and Balluffi did the same,[16] again on the classic Cu–Zn system: they referred to Hollomon's paper[9] where he had pointed out that Darken's or the activity gradient formalism were equally valid solutions, but the reference was only with regard to the activity data that were included in Hollomon's paper; not to assess the alternatives discussed within it. It almost appears to have been a 'policy decision'. LeClaire conceded that: 'for the few systems for which all the data are available, the results (i.e. Darken) are quite satisfactory, bearing in mind the difficulties of achieving high precision in measuring chemical diffusion coefficients.'[17] The Birchenall and Mehl activity gradient equation is now generally viewed merely as an evolutionary side branch.



a activation energy is always a constant increment over the average energy of the diffusing species on either side (Darken,[2] Manning[27]), generating flux equations (c), (d) and (f), *see* Appendix; *b* activation energy is always with reference to an independent, datum level at the saddle point (Birchenall and Mehl,[6] Guy,[10]) generating flux equation (b), and also (e) with the implied jump frequency being proportional to γ

2 Alternative approximations of the activation energy and their implications for the flux equation

It refused to die away completely, however, even if, for example, in the 1970s Siller and McLellan used it somewhat surreptitiously[18] as their basis for going on to offer an explanation for the eventual departure from the activity gradient predictions at very high carbon contents in austenitic iron.

In 1991, Liu *et al.* examined whether the improved knowledge of physics since the time of Hollomon's 1948 paper[9] could now answer the question it asked of which of the two formulations should be preferred.[19] They derived a relatively complicated equation that showed excellent agreement with the iron–carbon data, superior to either of these formulations. However, it can readily be shown that with increasing dilution, their equation tends to the activity gradient formula rather than to Darken's, as does also Siller and McLellan's. They disagreed with Siller and McLellan as to the reason for the departure from the alternative basis at high concentrations but, although they did not specifically mention this in their paper, their solution confirms the alternative as the better first approximation, perfectly valid to moderate concentration (5 at.-% for Fe–C).

Darken was originally criticised but then praised for offering a treatment that did not invoke or rely on a particular mechanism. (It appears to the author however, that this is equally true of the alternative.) Notwithstanding this, a mechanistic explanation of Darken's equation became prevalent in the textbooks; after all, there must be a valid mechanism associated with it. This is represented in Fig. 2. The activation energy that controls the jump frequency was stated to be modified by the difference between the non-ideal components of the chemical potentials on the atom planes either side of the saddle point in question, but was always a constant increment over the average of these values on either side: thereby, the overall jump frequency remains independent of concentration. Likewise, Birchenall and Mehl's activity gradient solution can be interpreted on such a basis, but whereby the activation energy is given by the difference between a datum, saddle point energy and whatever the actual energy was in any plane: thereby the overall jump frequency varies with concentration, and specifically, by being proportional to the activity coefficient. (Note: the diffusion coefficient is usually described in terms of an Arrhenius equation employing the activation enthalpy Q, with the temperature independent entropic term contained within a catchall pre-exponential factor. The jump probability, however, depends on the Arrhenius equation with this entropic term still included, i.e. in terms of the activation energy ΔG.)

In his own textbook with Gurry,[2] Darken rather understandably kept to his own formulation, although by this time he appeared much more relaxed about alternative treatments, happily conceding that the variability of diffusivity with concentration could not really be predicted because one simply does not know the true energy state of the saddle point. He even remarked (p. 463)[2] that the mobility (and thus diffusivity) appears to be proportional to γ in several systems.

Diffusivities or mobilities

In practice now, there seem to be two camps among those who model diffusive phenomena: those who stick to Darken and assume his equation is written in tablets of stone, and those who decry the diffusion coefficient formulation altogether, using instead the Onsager mobility formalism. The former tends to be the more commonly applied, and the latter does not have the Darken straightjacket, and lets the jump frequency (and thereby the underlying mobility) vary with concentration as however is seen fit, very much like LeClaire's recommendation regarding the diffusion coefficient. Indeed, from the commonly accepted definition of the diffusion coefficient, this should vary directly in proportion to the jump frequency, and the diffusion coefficient or Onsager mobility formalisms should be interchangeable. Moreover, a recognised approximation for the variation of jump frequency arising from the Bragg–Williams approximation is that it is very close to being proportional to the activity coefficient.[20,21] The respective formulae are included in the Appendix, where it can be seen that for a coordination number (number of equivalent neighbouring atoms) significantly greater than unity, which it must be in a simple lattice, the jump frequency is indeed proportional to the activity coefficient to a good approximation. Transferring this knowledge over to the diffusion coefficient formalism, we see that LeClaire's comment was probably right, that the activity gradient formalism is indeed probably the better one for all simple systems. But, contrary to Darken's eventual view that his was just one possible solution, his formula is generally taken to be the correct one. Moreover, contrary to Darken again, it is often assumed that the thermodynamic factor should be sufficient to account for the concentration dependence of diffusivity without any additional empirical fitting, to the extent that various workers have sought other means to try and explain why his formula falls far short of the experimental data for carbon in iron.[22,23]

Diffusion coefficient verses jump frequency

The Darken formalism is thus by no means written in tablets of stone as many presume, but there have been further variants of the standard flux equation to add to Fick's, Darken's and Birchenall and Mehl's. In an enigmatic aside in his classic textbook,[24] Christian stated that Fick's Law should really be written with the diffusion coefficient within the derivative (p. 349).[24] This stems from the definition of the diffusion coefficient being directly proportional to the jump frequency: the amount of 'stuff' moving must be the product of the amount of stuff available to move and the rate at which it does so. Therefore, one would indeed expect the net flux to depend on how this mathematical product varies with distance. Some researchers maintain this approach despite the antipathy of the general community,[25,26] usually expanded in terms of the jump frequency rather than expressed by a diffusion coefficient strictly defined as being proportional to the jump frequency (which is what most people assume, anyway). The CdD/dx term expected from the expansion of this variant of the flux equation is indeed suggested by the full, (weighted) random walk analysis of an arbitrary assemblage of atoms, but several texts claim that this somehow cancels out, and leaves a drift velocity term CV,[27] where it can easily be shown that V falls short of being dD/dx by a factor γ as above. But, again as above, others have effectively re-introduced this factor in the Onsager mobility formalism, and its transfer back into the realm of the diffusion coefficient formalism means that the drift velocity V should indeed approximate rather well to dD/dx.

Darken and Gurry remarked that metallurgists tend to remain unaware of relevant work in non-metallic materials.[2] With that in mind, this survey's net was cast a little wider, and it would appear that debate on the basic flux formulation has been ongoing elsewhere and the DC product form receives a more favourable press. In the field of electron flow in solids,[28] Landsberg addressed the question with his paper: 'Dgrad$C$ or grad(DC)?' and concluded that: 'provided one proceeds in an appropriate and consistent manner, either formulation is permissible.' He goes on to point out that 'the mathematical results also hold for atomic flow'. Collins and Takemori[29] however, did not agree. What is viewed by some as the 'heresy', J=–grad(DC), is declared to be 'the appropriate generalisation of Fick's law', and the 'often used' J=–Dgrad$C$ to be

'inconsistent'. The two formulations cannot generally be equated simply by particular choices of D. However, they did concede that if the average jump frequency between pairs of planes was independent of concentration, as per Manning[27] (and likewise all the general textbooks introducing atomic diffusion), one does recover the $D\text{grad}C$ form for that special case.

But let us reconsider the activity gradient formalism. The diffusion coefficient multiplying this gradient term in this case is simply that pertaining to infinite dilution, and is therefore necessarily independent of concentration. Therefore, we could move it inside the derivative term without upsetting the maths. We know that the diffusion coefficient houses the jump frequency term, and we are told that to a good first approximation this varies in proportion to the activity coefficient. The activity is just the product of the activity coefficient and the concentration. Let us 'detach' γ from C and 'stick' it to the D instead, D as a function of concentration being that at infinite dilution multiplied by the activity coefficient (via the jump frequency hidden inside D). What we then have is the flux given by the derivative of the DC product. Noting the forgotten γ term, this again becomes a mathematically equivalent representation.

A note of warning should be provided here, because this equivalence assumes isothermal diffusion. Within a temperature gradient the author would recommend the activity gradient formalism as the preferred starting point, invoking the temperature dependence of γ but not of the Arrhenius expression for the core diffusivity at infinite dilution. However, there are many further complications in this case, in the presence of a heat flux, beyond the scope of this review.

Conclusions

In summary, by noting an approximation for the variability of the diffusive jump frequency recognised by those who treat diffusion by the Onsager mobility formalism, we find that the standard Darken diffusion coefficient formalism is modified in such a way that it becomes identical with what are generally viewed as 'heretical' equations. It also appears that the debates were usually acrimonious, hampering proper discussion. Perhaps we have unearthed a resolution to the 60 year controversy concerning the formulation of the flux in simple, 'textbook level' systems, but it appears that this remains highly controversial.

Regarding complicated systems, highly sophisticated models exist including molecular dynamics and atomistic Monte Carlo that are making great progress.[30] However, with these, the flux is a result that can be inferred from the calculations rather than a formula that the analyses employ. Most materials scientists, though, embed the Darken equation within their models that apply diffusion to their system of interest, rather than modelling diffusion *per se*. They assume the mobility term embedded within the coefficient is independent of concentration, for simplicity and /or lack of data otherwise. Generally, they presume this is the best, simple approximation to make, but from perusing the literature and the available data, this is far from clear. Other, similarly simple formulas exist that could actually serve them better. However, for standard application to the many problems in materials science involving diffusion, perhaps LeClaire was right: just use the simple Fick's Law with the diffusion coefficient fitted as an empirical function of concentration, <u>if</u> the empirical data exist!

Appendix

Alternative equations for the diffusive flux *J*

(a) $J=-D\cdot\frac{\partial C}{\partial x}$ Fick; D is constant, i.e. equal to the value at infinite dilution D_0

(b) $J=-D_o\cdot\frac{\partial a}{\partial x}$ Birchenall and Mehl; a is the activity, γC, with γ as the activity coefficient referred to infinite dilution: $\gamma\rightarrow 1$ as $C\rightarrow 0$

(c) $J=-D_o\theta\cdot\frac{\partial C}{\partial x}$ Darken; θ is the thermodynamic factor, $\theta=\frac{\partial \ln a}{\partial \ln C}=1+C\frac{\partial \ln\gamma}{\partial C}$

$\theta\rightarrow 1$ as $C\rightarrow 0$

(Darken allowed the remaining D to be fitted empirically rather than assuming it constant at D_0.)

(d) $J=-D_o\cdot\frac{\partial C}{\partial x}+VC$ Darken; alternative representation of **(c)** with $V=-D_o\cdot\frac{\partial \ln\gamma}{\partial x}$

(e) $J=-\frac{\partial(DC)}{\partial x}$ Christian, DeHoff; reduces to **(d)** if $V=-\frac{\partial D}{\partial x}$ and tends to **(a), (b), (c)** and **(d)** as $C\rightarrow 0$

(f) $J=-L\cdot\frac{\partial\mu}{\partial x}$ Onsager, Darken; equivalent to **(c)** if the jump frequency within L is constant, or with D 'floating' in proportion to an arbitrary mobility, L

$L\rightarrow 0$ as $C\rightarrow 0$ $(L=CD/RT)$

The Missing Link:

The jump frequency $\Gamma=\Gamma_0\exp\left((z-1)c_f\varepsilon/kT\right)$

whereas $\gamma=\exp(zc_f\varepsilon/kT)$

therefore the jump frequency Γ (and thus D) is approximately proportional to the activity coefficient γ given that the co-ordination number z is significantly greater than unity.[12] (The concentration c_f here is expressed as the site fraction, ε is the nearest neighbour interaction energy, and k is the Boltzmann constant.) All the above can then be made equivalent, barring Fick (a).

For $D=D_0\gamma$, **(e)** clearly equals **(b),** and noting the relation $dy=y.d\ln y$:

(g)

$$D_0\frac{\partial a}{\partial x}=D_0\frac{\partial a}{\partial C}\cdot\frac{\partial C}{\partial x}=D_0\frac{a}{C}\cdot\frac{\partial \ln a}{\partial \ln C}\cdot\frac{\partial C}{\partial x}=D_0\gamma\cdot\theta\frac{\partial C}{\partial x}$$

it also equates to **(c)** and likewise **(d)** with appropriate insertion of the extra γ factor. Equation **(f)** is similarly rationalised, with $L=L_0\gamma$ according to its constituent γ being proportional to γ.

The versions of the second law are obtained simply by inserting the alternative first laws within the derivative in equation (3b). Thus, for example, **(b)** as above leads to

(h) $\frac{\partial C}{\partial t}=D_0\frac{\partial^2 a}{\partial x^2}$

Regarding the chemical interdiffusion, Darken's treatment[7] leads simply to multiplying equation (4) by his thermodynamic factor θ, which has to be the same for both elements

(i) $J=-\theta(C_A D_B+C_B D_A)\cdot\frac{\partial C_A^*}{\partial x}$

Regarding the DC product formulation, the following equation is derived upon following the same logic as described for Darken[13]

(j)

$$J = -(C_A D_A + C_B D_B) \cdot \frac{\partial C_A^*}{\partial x} - C_A C_B \cdot \left(\frac{\partial D_A}{\partial x} - \frac{\partial D_B}{\partial x} \right)$$

As before for the 'extra γ' or activity gradient formulation, changing the D variables to γD_0 terms yields the Darken expression **(i)** but with the D terms still being the products of the constant values at infinite dilution and the activity coefficients, γ.

* When transcribing for dC_B/dx, remember this is minus dC_A/dx.

References

1. A. Fick: *Ann. Phys. Chem.*, 1855, **94**, 59–86.
2. L. Darken and R. Gurry: 'Physical chemistry of metals'; 1953, New York, McGraw-Hill.
3. C. Tuijn: *Diffus. Defect Data Pt A*, 1997, **141–142**, 1–48.
4. P. Shewmon: 'Diffusion in solids'; 1989, Warrendale, PA, TMS.
5. L. S. Darken: *Trans AIME*, 1942, **150,** 157–171.
6. C. E. Birchenall and R. F. Mehl: *Trans. AIME*, 1947, **171**, 143–165.
7. L. S. Darken: *Trans AIME*, 1948, **175**, 184–201.
8. L. Onsager and R. M. Fuoss: *J. Phys. Chem.*, 1932, **36**, 2689–2778.
9. J. C. Fisher, J. H. Hollomon and D. Turnbull: *Trans AIME*, 1948, **175,** 202–215.
10. A. G. Guy: *Met. Trans.*, 1949, **185**, 607–610, and discussion, *Trans AIME*, 1950, **188**, 1024–1026.
11. C. Wells, W. Batz and R. Mehl: *Trans AIME*, 1950, **188**, 553–560.
12. R. P. Smith: *Acta Metall.*, 1953, **1**, 578–587.
13. A. A. Howe: *Scr. Mater.*, 2002, **49**, 619–623.
14. A. D. LeClaire: *Prog. Met. Phys.*, 1949, **1**, 306–379.
15. G. T. Horne and R. F. Mehl: *Trans AIME*, 1955, **203**, 88–99.
16. R. Resnick and R. W. Balluffi: *Trans AIME*, 1955, **203**, 1004–1010.
17. A. D. LeClaire: in 'Treatise on solid state chemistry, Volume 4, Reactivity of solids', (ed. N. B. Hannay), 1–57; 1976, New York/London, Plenum Press.
18. R. H. Siller and R. B. McLellan: *Met. Trans.*, 1970, **1**, 985–988.
19. W. J. Liu, J. K. Brimacombe and E. B. Hawbolt: *Acta Metall. Mater.*, 1991, **39**, 2373–2380.
20. T. Hill: 'An introduction to statistical thermodynamics'; 1962, Reading, MA, Addison-Wesley.
21. M. J. Brown *et al.*, in Proc. Conf. 'DIMAT 2004, 6th Int. Conf. on Diffusion in Materials', Krakow, Poland, July 2004, in press, AGH, Paper P1–6.
22. A McKee: Phys. Rev. B, 1980, **22B**, 2649–2657.
23. R. M. Asimow: *Trans. AIME*, 1964, **230**, 611–613.
24. J. Christian: 'The theory of transformations in metals and alloys'; 1965, Oxford, Pergamon Press.
25. R. T. DeHoff: *Trans. AIME*, 1968, **242**, 608–611, and discussion in 1969, **245**, 1825–1826.
26. R. T. DeHoff and N. S. Kullkarni: Mater. Res., 2002, **5**, 209–229.
27. J. Manning: 'Diffusion kinetics for atoms in crystals'; 1968, Van Nostrand.
28. P. T. Landsberg: *J. Appl. Phys.*, 1984, **56**, 1119–1122.
29. R. Collins and T. Takemori: *J. Phys.: Condens. Matter*, 1989, **1**, 3801–3820.
30. Y. Mishin, in Proc. Conf. 'DIMAT 2004, 6th Int. Conf. on Diffusion in Materials', July 2004', in press, Krakow, Poland, AGH, Paper I3.

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