Phenomenological Equations;

In chap.1 it was stated that in a binary phase, if the absence of a concentration gradient is an ~~def~~ adequate (sufficient, justifying) condition for a equilibrium, one is safe in using Fick's first law as a flux eq^n since the flux will go to zero as the system approaches equilibrium

This is applicable to many systems, and since the concentration is easily measured, it is commonly used.

However, $\frac{\partial c}{\partial x} = 0$ is a very restricted condition for equilibrium.

To gain insight into just what the limitations of this condition are, it is necessary to use a more general condition for equilibrium.

To obtain this general equation, One proceeds as follows.

For a given n-component system at equilibrium, the system can be uniquely determined by specifying T, P, μ_1, μ_2 ---, μ_{n-1} & ϕ,

where μ_i is the chemical potential & ϕ is any relevant scalar potential, e.g., electric potential.

If now the system is displaced slightly from the equilibrium, it seems more likely, and is certainly simplest, to assume that the rate of return to equilibrium is proportional to the ~~gradient of each of the potentials listed above~~ deviation from equilibrium.

And, until it is proved to be unnecessary, the flux of, say, component 1 is assumed to be proportional to the gradient of each of the potentials listed above.

Thus the most general equation for J_1 is

$$J_1 = -M_{11} \frac{d\mu_1}{dx} - M_{12} \frac{d\mu_2}{dx} \; - \; - \; - \; - \; -M_{1n} \frac{d\mu_n}{dx} - M_{1T} \frac{dT}{dx}$$

$$- M_{1P} \frac{dP}{dx} - M_{1\phi} \frac{d\phi}{dx} \qquad\qquad ---(1)$$

the equation for the flux of component 1, the flux of heat, etc, are given by comparable sums.

These are called the phenomenological equations since they stem from no model, but from the observed conditions of equilibrium.

A general discussion of the justification of these equations, as well as their simplification and manipulation can be found in de Groot.

Experimentally it is found that M_{1T}, $M_{1\phi}$ & M_{1P} are not zero, but for now we are interested only in the fact that in an isothermal, isobaric, isopotential system, J_1 is not only proportional to $d\mu_1/dx$, but may be proportional to $d\mu_2/dx$, $d\mu_3/dx$ etc, as well.

The chemical potential μ_i is defined by the equation

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_j} \qquad\qquad i \neq j$$

where G is the Gibbs free energy of the subsystem or phase. If the free energy of the total system is to be minimized at constant P & T, this is equivalent to the requirement that μ_i be the same in all parts of the system.

A complete, concise discussion of the application of the phenomenological equations to alloy diffusion is given by Bardeen & Herring. We shall discuss here only the assumptions required to obtain the flux equation assumed by Darken.

Consider a one-dimensional diffusion problem in a two component system. If we allow the possibility of a flux of vacancies (J_v) in addition to the fluxes J_1 & J_2 the flux equations are given by

$$J_1 = -M_{11} \frac{d\mu_1}{dx} - M_{12} \frac{d\mu_2}{dx} - M_{1v} \frac{d\mu_v}{dx} \qquad —(2)$$

$$J_2 = -M_{21} \frac{d\mu_1}{dx} - M_{22} \frac{d\mu_2}{dx} - M_{2v} \frac{d\mu_v}{dx} \qquad —(3)$$

$$J_v = -M_{v1} \frac{d\mu_1}{dx} - M_{v2} \frac{d\mu_2}{dx} - M_{vv} \frac{d\mu_v}{dx} \qquad —(4)$$

In any region where lattice sites are neither created nor destroyed the three fluxes are related by the equation

$$J_1 + J_2 + J_3 = 0 \qquad —(5)$$

If this is to be true for any value of each of the gradients, substitution of eq's (2,3,4) into (5) shows that we must have

$$M_{11} + M_{21} + M_{v1} = 0$$

$$M_{12} + M_{22} + M_{v2} = 0$$

$$M_{1v} + M_{2v} + M_{vv} = 0$$

For the equations written here, there is a set of reciprocity relations due to Onsager which state that $M_{ij} = M_{ji}$, so that $M_{12} = M_{21}$, $M_{v1} = M_{1v}$, & $M_{v2} = M_{2v}$.

Using all the equations b/w the M_{ij} gives

$$J_1 = -M_{11} \frac{d}{dx}(\mu_1 - \mu_v) - M_{12} \frac{d}{dx}(\mu_2 - \mu_v) \qquad -(6)$$

$$J_2 = -M_{21} \frac{d}{dx}(\mu_1 - \mu_v) - M_{22} \frac{d}{dx}(\mu_2 - \mu_v)$$

These are now the simplest equations which apply in general for a binary alloy where a vacancy mechanism is allowed.

If a vacancy mechanism does not operate, the vacancy conc" will be at equilibrium at all points, and $d\mu_v/dx$ will equal zero (as will μ_v).

To obtain Darken's flux equation, two additional assumptions must be made. These are

(1) that the vacancies are everywhere in thermal equilibrium or $\mu_v \simeq 0$, and

(2) that the off-diagonal coefficients M_{12} & M_{21} are essentially zero.

Listing these two assumptions in the first eq" of eq" (6) gives

$$J_1 = -M_{11} \frac{d\mu_1}{dx} \qquad -(7)$$

To relate D_1 to M_{11} in eq" (7), we equate our two expressions for J_1

$$J_1 = -M_{11} \frac{d\mu_1}{dx} = -D_1 \frac{dc_1}{dx} \qquad -(8)$$

If the force on an atom (F) was taken to be the gradient of the appropriate potential & v was the mean velocity of the atom when acted upon by F, the mobility B was given by the eq" $B = v/F$.

(used in stress assisted diffusion)

Combining the flux equations, eq" (8) gives

$$J_1 = C_1 v = B_1 F_1 C_1 = -B_1 C_1 \frac{d\mu_1}{dx} = -M_{11} \frac{d\mu_1}{dx} = -D_1 \frac{dc_1}{dx} \qquad -(9)$$

It is apparent that $M_{11} = B_1 C_1$, & that

$$D_1 = B_1 \frac{d\mu_1}{d \ln C_1} = B_1 \frac{d\mu_1}{d \ln N_1} \qquad —(10)$$

[the second equality in eq' (10) follows since if $\frac{C_1}{C} = N_1$ then $d \ln C_1 = d \ln N_1$]

The equation relating μ_i & N_1 is

$$\mu_1 = \mu_0 (T, P) + RT(\ln N_1 + \ln \gamma_1)$$

where γ_1 is called the activity coeff of 1. Thus

$$\frac{d\mu_1}{d \ln N_1} = RT \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right)$$

&

$$D_1 = B_1 RT \left(1 + \frac{d \ln \gamma_1}{d \ln N_1} \right) \qquad —(11)$$

The same sort of relation holds for component 2. In dilute sol'n, γ_1 is a constant.
(This follows from Raoult's law for the solvent & from Henry's law for the solute).

Thus in dilute or ideal solution, $D_1 = B_1 RT$, but in concentrated non ideal solutions the ratio $D_1 / B_1 RT$ will differ from unity. The sign & magnitude of the deviation will depend on the type & degree of non ideality.