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DIFFUSION AND THERMOKINETICS

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Abstract

Diffusion is a process of transport controlled by the random movement of mobile particles in fluid systems. The rate law of diffusion had been formulated by more different manners. The linear 'Fick-type' laws (the diffusion flux is proportional to the gradient of the concentration or activity) are based on experimental observations. The likewise linear force law (the diffusion flux is proportional to the chemical potential gradient) is one of the 'Ohm-type' laws of the irreversible thermodynamics. Both are in conflict with each other and with some general principles (equilibrium criteria, relativity theory). Applying the thermodynamic kinetic theory (called 'thermokinetics') it turns out that both linear laws are approximations of an exact but nonlinear equation the GeneralForce Law (GFL).

Keywords: thermokinetics, transports, diffusion, Fick's laws, irreversible thermodynamics.

1. Introduction

The diffusion is the migration of molecules in a mixture from point to point. The macroscopic properties of the system tend towards uniformity in composition or in the chemical potentials. First, we summarize the mean characteristics of the two linear diffusion equations, the Fick's and the Onsagerian ('Ohm-type') relations. For the shake of simplicity, the system studied here will be free of pressure- and temperature-gradient and long range external forces. The frame of reference of the molecular motions is chosen so that the convective part of the transport always be zero (e.g., equimolar center). They differences in the approaches stand in that how to answer the questions:

What is the process rate?
What is the driving force?
What is the force law?
What is the motionless, rest state?

2. The Diffusion Flux

The more general definition of mass flux has the form:

$$\mathbf{J}_i = \mathbf{w_i} \cdot C_i\,, \tag{1}$$

where $\mathbf{J}_i$ is the flux of the i'th component, (moles/m^{2}s)
C_i is the i'th concentration (moles/m^3)
$\mathbf{w}_i$ is the mean speed of the particles i (averaged on all particles), m/s

(as if all particles would move with a common speed $\mathbf{w}_i$).

3. Fick's Laws

The regularities of the diffusion process were first investigated by FICK (1856) [1]. His main conclusion were: the diffusion flux vector is proportional to the gradient of the concentration

$$\mathbf{J}_i = -D_i \cdot \text{grad } C_i \qquad \text{(Fick I.)} \tag{2}$$

where D$_i$ is the diffusion coefficient (m^2/s)

D is in most cases concentration-independent with a very good approximation. Though the diffusion processes of different components may show interdependences (e.g. 'binary diffusion') , to this problem we will not go into details. It turned out that this law is valid exactly in ideal mixtures. In non-ideal systems C_i is to replaced by a modified concentration, the 'activity' or, at gases, the partial pressure by the 'fugacity'. However, in most practical cases, the linearity in grad C_i is a good approximation. [2]–[7].
Fick's law can be read as:

a. The rest state is at uniform concentration (grad $C_k = 0$).
b. When the concentrations get non-uniform, the migration of the molecules 'comes into being'.
c. At non-steady conditions the time change of the concentration is proportional to the second derivative of the concentration-distribution. Assuming a concentration-independent D_k

$$\partial C_k/\partial t = D_k \cdot \text{div grad } C_k \qquad \text{(Fick II.)} \tag{3}$$

called 'Fick's Second Law', a linear differential equation of parabolic type.

4. The Force Law

The foundations of a general thermodynamic process theory (called 'Irreversible Thermodynamics') were laid down by Lars ONSAGER in 1931 [8]. ONSAGER is based on the linear phenomenological laws of various process rates: the viscous flow (NEWTON, 1687), heat conduction (FOURIER, 1822), electric conductivity (OHM, 1826) and the diffusion (Fick). All linear process rate relations are formulated in an 'Ohm-type' form: The fluxes are linear homogeneous functions of the thermodynamic 'forces'. The forces are gradients of the appropriate 'potentials'

(F_i), the temperature at heat conductance, the chemical potentials at mass flows, etc. The rest state is the equilibrium state, at uniform thermodynamic potentials (not necessarily identical to the uniform concentration). At equilibria the fluxes and the 'forces' (differences or gradients of the potentials F) vanish. In our case, the diffusion rate ($\mathbf{J}_k$ the same as in Fick's law) is proportional to the gradient of the appropriate chemical potential [9]–[12].

$$\mathbf{J}_i = -L_i \cdot \operatorname{grad} \mu_i \qquad \text{(Ons.)} \tag{4}$$

The (assumed constant) factors of proportionality called the 'phenomenological coefficients' (L) The concentration and the chemical potential are in non-linear (logarithmic) relation.

$$\mu_i = \mu_i^0 + \mathrm{RT} \cdot \ln C_i, \tag{5}$$

or

$$e^{\frac{\mu_i}{\mathrm{RT}}} = e^{\frac{\mu_i^0}{\mathrm{RT}}} \cdot C_i. \tag{6}$$

In an ideal solution

$$\mu_i^0 = \text{const}. \tag{7}$$

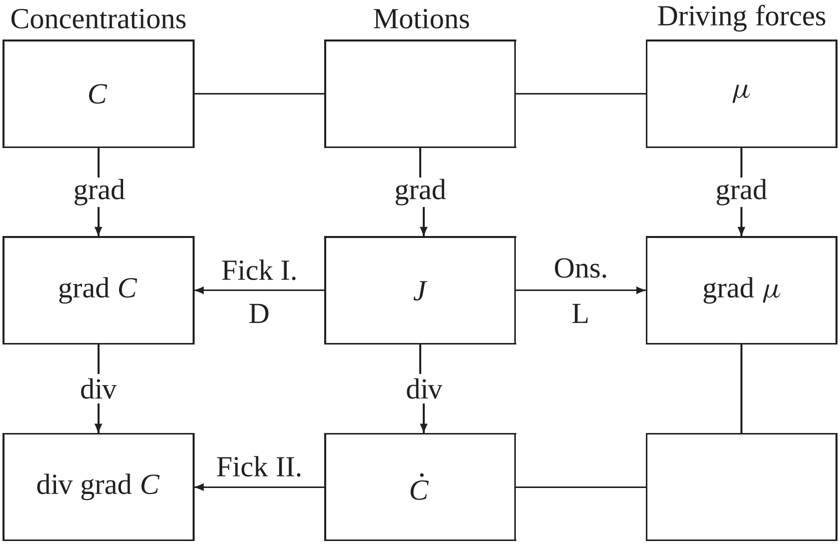

Table 1. Fick's and Onsager's laws. Connections of the basic quantities.

5. Problems, Contradictions

Formally, the rate equations in the Fick- and the Onsager-representation (CIT) are of similar form, apart from the physical content of the force-parameter (C or a and μ). The two theories, however, conflict in more points. Moreover, both have inconsistencies with some general laws (thermodynamics, relativity theory). The main problematic points are:

a. The problem of the velocity.

Both theories (Fick and Onsager) define the process rate (**J**) as the average flux of the molecules in question. In this sense, the average velocity vector of the particles is

$$\mathbf{w} \equiv \mathbf{J}/C \quad \text{(m/s)}. \tag{8}$$

This interpretation, however, leads to more contradictions.

Example. Regard a layer separating two solutions (I. and II.). The solute molecules enter on a left side boundary, diffusing towards the right side and leaving it for the second solution (*Fig.* 1). Keeping steady boundary concentrations (C_I and C_{II} and $C_{II} \approx 0$) a steady state will set up.

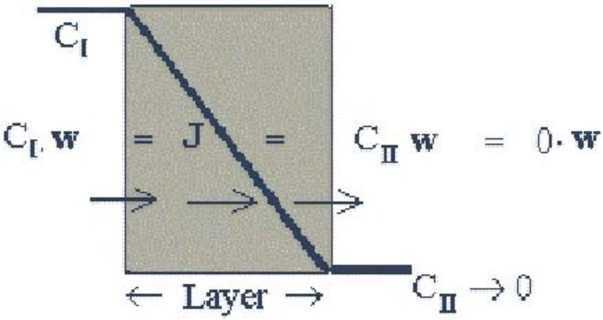

Fig. 1. Steady diffusion through a layer. First contradiction: unlimited velocity.

Here, the layer is regarded to be at rest. Flux **J** is a vector directed perpendicular to the boundaries. At steady state **J** must have the same uniform value inside the whole layer. But, when C_{II} tends to zero, the velocity **w** (defined as $\mathbf{J}/C$), must increase beyond all limits. This contradicts all rational considerations. Similar problem arises using *Eq.* (4)

When $C \to 0$ then $\mu \to -\infty$ and $L \to 0$ what is a nonsense as well.

b. The problem of infinite speed of action

Relation Fick II. is a differential equation of parabolic type. This fact leads to the consequence that a finite perturbation at a given place and time results in a finite change at a finite distance within an infinite small time period [13]. But, according to the relativity theory, no action can propagate with a velocity greater than the (finite) speed of light [14].

c. Thermodynamic inconsistency

The principle of transitivity of equilibrium requires that at equilibrium all independent thermodynamic potentials (e.g., the temperature and chemical potentials) must equilibrate, their gradients vanish. In the sense of Fick's law the fluxes vanish when the concentrations (but not exactly the chemical potentials) equilibrate. Consequently, Fick's laws do not harmonize with thermodynamics (while Onsager's relations do). Experimental proofs: In Fick's equation the diffusion constant (D), in Onsager's relation L is supposed to be constant parameter. Comparing D and L parameters:

$$L_i = D_i \cdot C_i. \tag{9}$$

If L_i would be constant against C_i, then the Onsager's relation would be correct and if D_i, then Fick's equation. A number of experiments have proved that the Fick equation is the correct one. [3]–[4].

Conclusion: neither Fick's nor Onsager's rate equation is the exact general form to describe diffusion processes. It turned out that neither of the two representations can be reformed. A radical change must be made. The flux, the driving force and the force law must be otherwise formulated.

6. Absolute and Net Fluxes

Most problems are consequences of the fact that the fluxes **J** have been defined in a too simplified way, the mode of averaging does not allow to take the dynamics of equilibrium (self diffusion) into account. It is well known that the diffusion flux observed results of the fact that at a given place the number of particles migrating in a forward direction differ of those migrating in a opposite, backward direction. It is consequence of a spatial deformation of the internal migration process rates. The kinetic activity is measured by the 'absolute rate', a local scalar property.

The absolute value of the (thermal) velocities of the particles can be defined as [7]

$$\overline{u}^2 = \overline{u}_x^2 + \overline{u}_y^2 + \overline{u}_z^2. \tag{10}$$

The square root of the average of u^2 will be denoted as u.One must stress that u is a mean thermal speed always less than the speed of light. The average absolute flux (the ‘traffic density’) is the average

$$j = u \cdot C \qquad (\text{moles }/\text{m}^2 \cdot \text{s}) \tag{11}$$

where C is the concentration of the mobile particles.

The absolute flux density is in close relation with the kinetic energy density density and with the pressure as well.

$$j = C \cdot \sqrt{\frac{2 \cdot E_{\text{kin}}}{M}}, \tag{12}$$

where M is the molar mass of the particles in question.

The pressure is the traffic density of the momenta

$$P = j \cdot p, \tag{13}$$

where p is the average momentum of the particles.

Forward and backward absolute fluxes

For describing the mechanism of diffusion there is practical to choose a reference (y, z) plane of unit area normal to the macroscopic diffusion flow (coordinate x). The absolute flux can be thus splitted to a ‘forward’ (positive velocity) and a ‘backward’ part (negative velocity component) (called by Bird: ‘inward’ fluxes):

$$j_x^{(+)} = u^{(+)} \cdot C^{(+)} \tag{14}$$

$$j_x^{(-)} = u^{(-)} \cdot C^{(-)} \tag{15}$$

and

$$j = j^{(+)} + j^{(-)}, \tag{16}$$

where $C^{(+)}$ is the concentration of the particles moving in a positive (forward) direction and

$C^{(-)}$ is the concentration of the particles moving in a negative (backward) direction.

$u^{(+)}, u^{(-)}$ are the square roots of the average of the squares of the x-directed velocities

$$u^{(+)} = u^{(-)} = \frac{u}{\sqrt{3}} \tag{17}$$

$j^{(+)}$ is the number of moles passing the $y \cdot z$ plane per unit time in a $+x$ direction

$j^{(-)}$ is the number of moles passing the $y \cdot z$ plane per unit time in a $-x$ direction.

(Other counter-processes: input/output, income/outcome, export/import etc.)

$j^{(+)}$ and $j^{(-)}$ are time reversal pairs and there is thus possible to apply the appropriate law, the law of detailed balance. At equilibrium the non-zero reverse processes are exactly balanced.

$$j_{\text{eq}}^{(+)} = j_{\text{eq}}^{(-)}, \tag{18}$$

$$C_{\text{eq}}^{(+)} = C_{\text{eq}}^{(-)} = C/2. \tag{19}$$

In the sense of the 'local equilibrium' hypothesis there exist the appropriate chemical potentials

$$\mu^{(+)} \quad \text{and} \quad \mu^{(-)}.$$

Introducing the scalar local quantity j, the system of the fundamental local scalar properties are completed to three and with the differences (or gradients) and the second derivatives (div grad) to nine. The main relationships connecting them are derivable from the first three [15]-[18].

$\mu(C)$	(Equation of state, thermostatics)
$j(C)$	(Rate relation, Mass-Action type, Fick)
$j(\mu)$	(Rate relation, force law type).

The $\mu(C)$ relation

Ideal mixture :

$$\mu = \mu^0 + \text{RT} \cdot \ln C, \tag{20}$$

or

$$e^{\frac{\mu}{\text{RT}}} = e^{\frac{\mu^0}{\text{RT}}} \cdot C, \tag{21}$$

where μ^0 is the constant part of μ.

In non-ideal phase, C is to be replaced by the activity, or, the partial pressure to fugacity.

The $j(C)$ type rate equations

These kinetic equations are the so-called 'Mass Action Law' types of the process rates. (The rates are proportional to the amounts of the participants). $j(C)$ is the source of the Fick type equations (might be called, 'Fick's 0' relation).

$$j = u \cdot C. \tag{22}$$

C means here the concentration of the particles. If only a part of them ismobile, a constant factor can be needed. As seen, it is essentially the definition of j.

The $j(\mu)$ force law is non-linear

The two former types of relationships, $\mu(C)$ and $j(C)$ demand, that the appropriate form of the force law be an *exponential* function. The 'Force Laws' connecting the fundamental kinetic properties, the (absolute) motions (j) and the driving potential (F) are typically exponential

$$j = j^0 \cdot \exp(F)$$

$j(F)$ **transport relations are non-linear!**

In our case the is the appropriate potential the chemical potential

$$F = \frac{\mu}{\mathrm{RT}}$$

$$\text{General Force Law} \qquad \boxed{j = j^0 \cdot e^{\frac{\mu}{\mathrm{RT}}}} \qquad \text{(GFL)} \tag{23}$$

where j^0 is a constant factor

$$j^0 = u \cdot C^0 \cdot e^{-\frac{\mu^0}{\mathrm{RT}}} = \text{const.} \tag{24}$$

C^0 is the sum of the concentrations in a mixture.

GFL is the rate law of internal migration both in equilibrium and non-equilibrium body.

It harmonizes with Fick's law but differs from the (linear) Onsagerian form. The force factor $e^{\frac{\mu}{\mathrm{RT}}}$ is called by Guggenheim: 'absolute activity'.

7. Non-Equilibrium System

Net fluxes, gradients, characteristic length

Diffusion flux J is observed if the counter-parts of the absolute flux are not balanced.

J is the difference of the reverse absolute fluxes, ('net' flux):

$$J = j^{(+)} - j^{(-)} \neq 0 \qquad (C^{(+)} \neq C^{(-)}). \tag{25}$$

Due to fixed space direction (x), vector $\mathbf{J}$ reduces to a scalar unidirectional J_x

$$\mathbf{J} = (J_x, 0, 0) \tag{26}$$

$$J_x = u_x \cdot (C^{(+)} - C^{(-)}) = -u_x \cdot \Delta C \tag{27}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\Delta J_x = u_x \cdot \Delta(\Delta C) \tag{28}$$

which is originally a difference-, and not a differential-equation.

For macroscopic description a very good approximation can be used: the differences are proportional to the gradients

$$\Delta \approx \lambda \cdot \frac{\mathrm{d}}{\mathrm{d}x} \tag{29}$$

and

$$D = u \cdot \lambda, \tag{30}$$

where λ is a ‘characteristical length

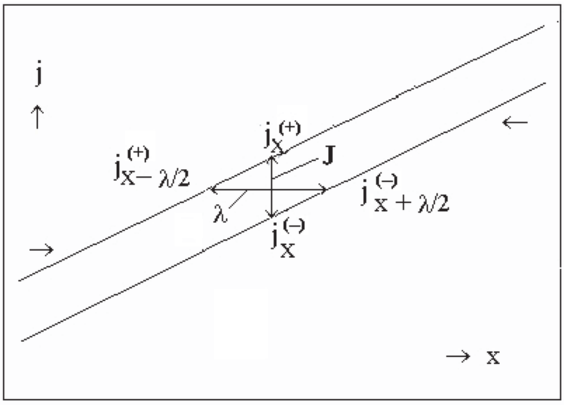

Fig. 2. Relations of J, $j^{\rightarrow}$ and $j^{\leftarrow}$, grad j and λ

The difference equations can thus be approximated with differential equations:

$$J_x = -D \cdot \frac{\mathrm{d}C}{\mathrm{d}x} \qquad \text{(Fick I.)} \tag{31}$$

$$\mathrm{d}C\mathrm{d}t = D \cdot \mathrm{d}^2C(\mathrm{d}x) \qquad \text{(Fick II.)} \tag{32}$$

$$J_x = \left(\lambda \cdot j^0\right) \cdot e^{\frac{\mu}{\mathrm{RT}}} \cdot \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mu}{\mathrm{RT}}\right) \qquad \text{(Ons.)} \tag{33}$$

$$J_x = \lambda \cdot j^0 \frac{\mathrm{d}}{\mathrm{d}x}\left(e^{\frac{\mu}{\mathrm{RT}}}\right) \qquad \text{(GFL)} \tag{34}$$

The characteristic length λ is an important parameter of processes where displacement and interaction of the counter-fluxes takes place. In general, it measures the ratio of the two opposite effects. λ can be 10^{-10} m or equal to the free path in gases. A distant relative of it is the HETP at chromatography or fractional distillation operations.

The relations can be illustrated as follows:

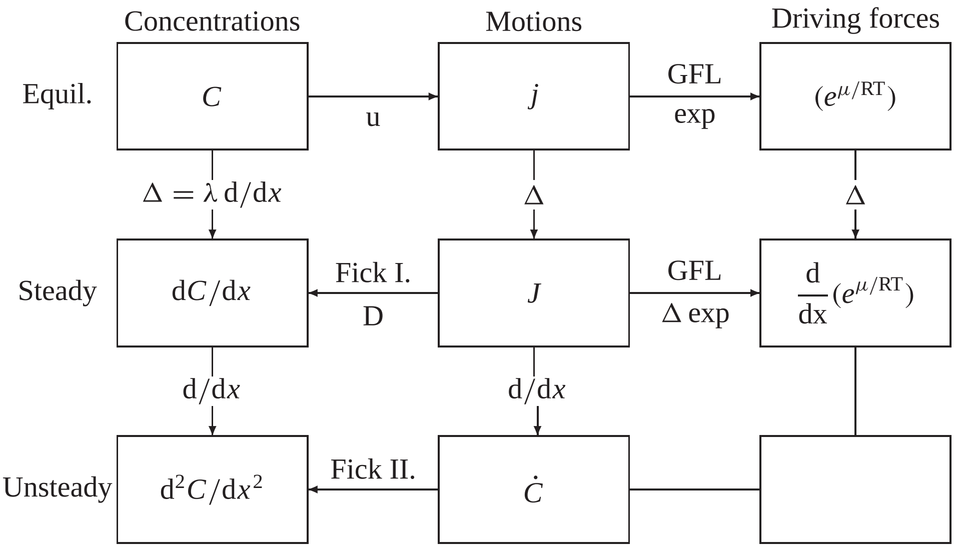

Table 2. Derivation of the diffusion equations from GFL

8. Conclusions

Applying the thermokinetic theory on transport processes one could find the original form of the diffusional process equations. This relation, called the 'General Force Law' (GFL) is free of contradictions.

GFL is non-linear

Both linear or quasi-linear laws (Fick, Onsager) are derivatives of GFL

The derivation implies approximations (differences → differentials, exponential → linear).

All contradictions burdening the 'linear' laws are consequences of the approximations.

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