THERMOKINETICS
An introduction

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Abstract

A new theory called "Thermokinetics" is explained which completes former classical theories, as "Thermostatics" and "Non-equilibrium Thermodynamics". Thermokinetics is based upon the concept of mutual "inward" process rates. Canonical forms of rate equations are formulated and a Symmetry Principle of Inward Rate Equations is presented. The canonical rate equations make possible a reformulation of the linear phenomenological transport equations, and new interpretations for the Onsager-relations and the transport coefficients. A modified and completed "three-pole" scheme of the fundamental properties and relations is drawn.

Introduction

The two main theories of macroscopic systems, thermostatics and (non-equilibrium) thermodynamics provide an exact and complete treatment of the great majority of systems and processes. Nevertheless, there are some phenomena which could not be interpreted properly with the concepts of the two theories mentioned.

Such phenomena are first the dynamic properties of equilibria: the extent of "reversibility", the intensity of compensated mutual exchange processes.

Second, the construction of a general macroscopic kinetic theory was difficult due to the lack of a universal, "canonical" formulation of rate equations.

Third, thermodynamics can treat only near-equilibrium situations properly. The way of the extension to far from equilibrium systems induces serious complications.

Most of these problems can be circumvented by founding a theory on the concept of the mutual "inward" process rates which enables a third additional theory, "thermokinetics", to be constructed.

Thermokinetics, thermostatics and thermodynamics together form a complete and symmetrical theory of macroscopic systems and processes and provide new tools for solving problems so far too complicated and difficult, for example in far from equilibrium and non-linear systems.

In this paper the theory is applied to elementary "one step" processes (discontinuous systems), while the extension to diffusion-type ("multi-step") processes and chemical reactions will be discussed in other papers.

Inward fluxes

Thermokinetics is based upon the existence of mutual "inward" rates of fluxes or processes, respectively.

As is known, all thermodynamic systems are composed of a great number of similar microscopic elementary systems, e.g. molecules. Similarly, all thermodynamic processes are the resultants of elementary events on the microscopic-molecular level. For example, at a liquid surface a molecular process can result in a molecule leaving the liquid phase. The sum of all these processes results in an evaporation mass flux (j'). Such fluxes will be called "inward fluxes". On the same surface, the inverse molecular processes can proceed simultaneously with the reverse result: molecules enter the fluid from the vapour phase. The macroscopic sum of these inverse mass transport processes results in a condensation flux (j''). Another example is: decomposition of an electrode process into an anodic and a cathodic inward exchange current.

The role of inward fluxes is also conceivable for heat transfer: an energy change takes place on the molecular level via interactions between molecules of the two phases at the interface. Some of these interactions result in energy gain for phase (Sy'), other interactions for the other phase (Sy''). The macroscopic sum of the energy transfer

$$Sy' \rightarrow Sy''$$

is an inward energy flux j'_u and the sum of the inverse processes

$$Sy' \leftarrow Sy''$$

is the inverse inward energy flux j''_u .

These mutual inward fluxes exist also in equilibrium. In such a case, however, these processes do not contribute to the entropy production and are not to be estimated by observing the changes in some properties of the systems. They are measured indirectly in many cases (similarly to the indirect evaluation of mass transport in general). Such methods are e.g. isotopic indication or, in electrode kinetics, analysing the current-voltage characteristics. Statistical calculations often refer to these inward process rates. (The word "inward" was taken from a work of this area [1]).

Equilibrium systems. A three-pole structure

Classical thermostatics deals with two fundamental groups of state parameters. These are the extensities (E_i) and the appropriate "potentials" (F_i). When dealing with "local" systems, the role of the extensities is taken over by the appropriate "densities" or concentrations (c_i):

$$c_i \equiv \lim_{V \to 0} \left(\frac{E_i}{V} \right). \tag{1}$$

The potentials are defined as

$$F_i \equiv \left(\frac{\partial S}{\partial E_i} \right) = \left(\frac{\partial c_S}{\partial c_i} \right). \tag{2}$$

where S is the entropy and c_S the entropy-density. In order to complete the characterisation of equilibrated (two-phase) macro-systems, we introduce the inward flux densities (j_i) as a third fundamental group.

In this paper we treat "one-step" processes only. (Applications: transfer from one phase to another, free flow of molecules in a Knudsen-gas, chemical transformations).

These three sets of quantities are of equal importance:

$$\underline{\uparrow c_i \leftrightarrow F_i \leftrightarrow j_i . \uparrow}$$

Three kinds of constitutive relationships exist between them (Fig. 1).

a) The $F_i \leftrightarrow c_i$ relationships are the fundamental constitutive equations of thermostatics. Some of them are:

$$\frac{\mu_k}{T} = \frac{\mu_k^\circ}{T} + R \ln c_k \qquad \text{(ideal system)}$$

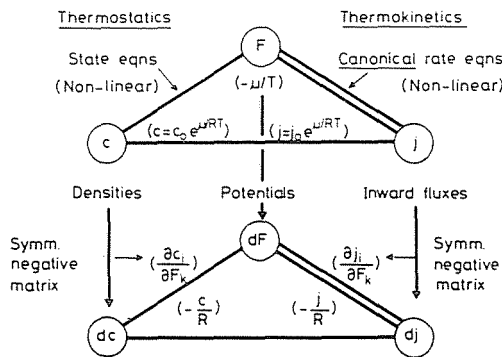$$\frac{p}{T} = Rc \qquad \text{(ideal gas)}$$

Fig. 1. Three-pole structure of equilibrium properties

b) The $j_i \leftrightarrow c_i$ rate equations are familiar in many processes. e.g. a mass flow against a fluid surface from an (ideal gas) vapour phase can be written as

$$j'' = j_{\text{cond}} = \frac{1}{2} u \cdot c \qquad \text{mole/m}^2\text{s}, \tag{3}$$

where u means the average velocity component perpendicular to the surface. (u is proportional to the square root of the temperature).

Using this interpretation, the inverse rates of the same process (here, the rate of evaporation) have dissimilar forms, e.g.

$$j' = j_{\text{evap}} = K' \cdot T^{n'} \cdot \exp\left(-\frac{\Delta H_{\text{vap}}}{RT}\right). \tag{4}$$

where an unlike temperature-dependence is remarkable.

In most cases, rate equations of this kind are not consistent in the sense that the set of independent variables is a mixed one: some of them are densities while others are potentials (e.g. temperature). Most chemical rate equations show such a mixed representation.

c) The $j_i \leftrightarrow F_i$ "canonical" equations may be called the "*constitutive relations of thermokinetics*". These show some important general features and are capable of making connections with Onsager's non-equilibrium thermodynamics. In mass trasfer processes, a typical form of the canonical rate equations is

$$j = j^0 \cdot \exp\left(\frac{\mu}{RT}\right). \tag{5}$$

and j^0, in general, varies with the temperature as follows:

$$j^0 = K \cdot T^n \exp\left(-\frac{E}{RT}\right). \tag{6}$$

Some of the parameters in (5) and (6) depend on the properties of the bulk, others (e.g. the activation energy, E) measure the permeabilities of the boundary.

The constitutive equations (similarly to the thermostatical state equations) are in general non-linear. As it will be shown later, the set of canonical inward rate equations involve all the information about the transport process rates in linear and non linear situations.

Equilibrium criteria. Principle of detailed balance

Contrary to non-equilibrium thermodynamics, thermokinetics deals also with equilibria. Inward fluxes not vanishing in equilibrium provide it with a dynamic character ("dynamic equilibrium"). The intensities of the inward rates

measure the "intensity" or "reversibility" of the equilibrium. (An electrode-electrolyte equilibrium is called more or less "reversible" with higher or smaller exchange currents.)

Equilibrium is specified in various ways:

a) Thermostatics: some fundamental thermodynamic quantities corresponding to the existing constraints have extreme values. In a closed system, entropy should have a maximum value. [2, 3]

$$S = \text{maximum} \qquad (7)$$

b) Equilibria can also be characterized by the concepts of non-equilibrium thermodynamics. According to this theory, in equilibria all thermodynamic forces (X_i) vanish [4, 5]

$$X_i = F_i'' - F_i' = 0 \qquad (i = 1, 2, \ldots, n). \qquad (8)$$

c) In thermokinetics equilibria are characterized by the law of "Detailed Balance" (DB): in equilibria the inverse inward fluxes are equalized in all details:

$$j_i' = j_i'' \qquad (i = 1, 2, \ldots, n). \qquad (9)$$

(Inward fluxes are considered positive in the direction "out").

In equilibria, a, b, and c are satisfied simultaneously. Comparing b and c, interesting conclusions can be drawn as to the inward rate equations. [6, 7]

Symmetry of the inverse inward rate equations

As we have seen, in equilibria both the potentials and the partial rates show transitivity.

$$F_i' = F_i'' \qquad (= F_i)$$

$$j_i' = j_i'' \qquad (= j_i) \qquad (DB).$$

Let us now change any of the potentials F_k by ΔF_k equally in both equilibrium systems so that a new equilibrium characterized by new potentials

$$F_k' + \Delta F_k' = F_k'' + \Delta F_k'' \qquad (= F_k + \Delta F_k)$$

is established.

As a consequence of the law of DB it must be valid for the new fluxes that

$$j_i' + \Delta j_i' = j_i'' + \Delta j_i'' \qquad (= j_i + \Delta j_i).$$

Supposing that both ΔF_k and Δj_i are small:

$$\Delta j_i' = \sum_k \left(\frac{\partial j_i'}{\partial F_k'} \right) \Delta F_k = \sum_k \left(\frac{\partial j_i''}{\partial F_k''} \right) \Delta F_k = \Delta j_i'' \qquad (10)$$

or, by omitting the distinction between j_i' and j_i'', F_k' and F_k''

$$\Delta j_i = \sum_k \left(\frac{\partial j_i}{\partial F_k} \right) \Delta F_k. \tag{11}$$

As the values of F_k' s may be selected arbitrarily, and (8) and (9) must be valid simultaneously for all equilibria, the flux rate equations must have the
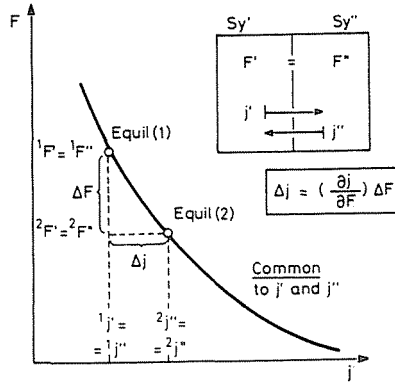

Fig. 2. Inward process rates in various equilibria (1 and 2). Canonical $(j \leftrightarrow F)$ relations are common to the inverse inward processes

same functional form for the inverse rates j_i' and j_i'' supposing that the rate equations are formulated canonically (see Fig. 2).

$$j_i' = f_i(F_1', \ldots, F_n') = f_i(F_1'', \ldots, F_n'') = j_i''. \tag{12}$$

This fact may be surprising if the transport takes place between phases of different properties (e.g. a liquid and its vapour).

Non-equilibrium systems. Net fluxes

Let us now consider a system in non-equilibrium. In subsystem Sy' the potentials are F_k' and the appropriate fluxes are j_i'. Let us now change the potentials by ΔF_k in subsystem Sy'' only. Consequently, the inward fluxes j_i'' change too.

The situation may be represented as shown in Fig. 3 and 4.

Due to the disequilibration of the inward fluxes, "net" transport rates arise (J_i)

$$J_i = j_i' - j_i'' = -\Delta j_i. \tag{13}$$

Fig. 3. Three-pole structure of non-equilibrium systems

Fig. 4. Inward process rates in non-equilibrium systems

These net fluxes are the fundamental fluxes in the Onsager-theory. Contrary to the equilibrium discussion in chapter 5, symbol Δ means here a difference and not a change. Similarly, ΔF_k means a difference of the potential F_k, which is equal to the $k'th$ thermodynamic force (X_k) and not to the variation of F_k inside one (or both) subsystem.

$$X_k = F_k'' - F_k' = \Delta F_k. \tag{14}$$

In the vicinity of equilibrium, where

$$\frac{\Delta j_i}{j_i} \ll 1 \tag{15}$$

according to (11) and (14)

$$J_i = -\Delta j_i = -\sum_k \left(\frac{\partial j_i}{\partial F_k}\right) X_k \tag{16}$$

which is equivalent to the known set of linear phenomenological equations of L Onsager:

$$J_i = \sum_k L_{ik} X_k. \tag{17}$$

In the sense of Thermokinetics, these equations form a Jacobian set of full differentials where

$$L_{ik} = -\left(\frac{\partial j_i}{\partial F_k}\right) = -\left(\frac{\partial j_k}{\partial F_i}\right) = L_{ki} \tag{18}$$

(18) forms an important link between Thermokinetics and the Onsager-Thermodynamics which allows a deeper insight into the physical meaning of the phenomenological coefficients. For example, in the case of mass transport from one phase to another, L_{mm} shows not only the extent to which the interface is permeable to some species, but also the variation of the inward mutual permeation flux j_m with respect to the variation of the quantity $(-\mu/T)$. By heat transfer, the transport coefficient is equal to the negative derivative of the inward heat transfer flux with respect to the reciprocal temperature $(1/T)$.

The physical meaning of the cross effect is, in this sense, that the inward transfer flux of the i'th quantity varies not only with the variation of the i'th but also with another $(k'$th) potential too. A mass flow carries heat if the inward mass flux is temperature-dependent.

In general, *far from equilibrium* approximations (10) and (15) are not valid. Such problems are common in chemical kinetics. In such cases, use of the linear Onsager-theory is very difficult, what is more, the use of the concept "force" (Affinity) looses its meaning. The fluxes are to be expressed as functions of the potentials and not of potential differences. The right way is not to extend the linear theory (with forces) but turning back to Thermokinetics without the linear approximations. For example with (5) a mass transport rate is

$$J_m = -\Delta j_m = -j_m^0 (e^{\mu'/RT} - e^{\mu''/RT}).$$

Summary of results

Based upon the mutual "inward" fluxes and their rate equations, a three-pole structure and three fundamental sets of relationships are presented. One of them, not commonly used up to now, has a particular importance. This is the set of rate equations of the type $j_i \leftrightarrow F_i$ called "canonical" rate relations. It has been shown that, due to the principle of detailed balance, the inverse canonical inward rate equations must have the same functional form and common values of the constant parameters in them.

It has also been shown that these relationships may be regarded as sources of all thermodynamic transport equations including that of Onsager's phenomenological rate equations.

In terms of this theory the familiar rate relations may be reformulated. The phenomenological linear relations are equivalent to a set of Jacobian differential relations of the inward rate equations and Onsager's $(dj_i \leftrightarrow dF_i)$ reciprocity relations lead to symmetry relations of the derivatives of the inward fluxes with respect to the potentials. Far from equilibrium in nonlinear cases, rate relations of the type $J_i \leftrightarrow X_k$ lose their sense and relations of J_i and F'_k and F''_k are meaningful only.

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