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GENERAL THEORY OF HEAT AND MASS EXCHANGE
 IN CHEMICALLY REACTIVE SYSTEMS IN MECHANICAL
 EQUILIBRIUM WITH ELECTRIC FIELD WITHIN
 THE FRAMEWORK OF THERMODYNAMICS OF IRREVERSIBLE
 PROCESSES

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General analysis of the effects of chemical reactions on the processes of heat and mass transfer has been the subject of many investigations (see literature cited in [1]). Such an analysis for mechanical equilibrium systems in symmetrical form was given in [2]. In the present article it is shown that a description of chemical processes in the special meaning of the term can be carried out independently of heat and mass transfer.

The processes which take place in a mechanical equilibrium (at rest) system consisting of k chemical components K_i ($i, j = 1, \dots, k$), among which r independent reactions R_s ($s, t = 1, \dots, r$) occur, are described by k continuity equations,

$$\rho \frac{\partial c_i}{\partial t} + \operatorname{div} I_i = \sum_s m_i \nu_{is} \theta_s, \quad (1)$$

where, in addition to other notation, c_i is mass fraction; I_i is diffusion flow; m_i is molecular weight, g/mole; θ_s is the rate of R_s , mole/cm³·sec; ν_{is} is stoichiometric coefficient of K_i in R_s . Moreover, we have the mechanical equilibrium condition

$$\nabla p = \rho z \mathbf{E}, \quad (2)$$

where z is the free charge per unit of mass, as well as the energy equation which in usual notation is given by

$$\partial \rho e / \partial t + \operatorname{div} \mathbf{q} = (\mathbf{j} \mathbf{E}). \quad (3)$$

The system (1)-(3) is supplemented by the Gibbs relation,

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$$d\varepsilon + pdV = Tds + \sum_i \mu_i dc_i, \quad (4)$$

where μ_i is chemical potential per unit mass, and also by the condition that the electrical field is a potential one,

$$\mathbf{E} = -\nabla\varphi \quad (5)$$

and, finally, by the Poisson equation,

$$\operatorname{div} \mathbf{D} = \rho z. \quad (6)$$

In addition, the continuity condition of the electric current is given in its low-frequency approximation by

$$\operatorname{div} \mathbf{j} = 0. \quad (7)$$

From (1)-(4) there follows the equation for the entropy,

$$\rho \frac{\partial s}{\partial t} + \operatorname{div} \frac{1}{T} \left(\mathbf{q} - \sum_i \mu_i \mathbf{I}_i \right) = (\mathbf{q}\nabla) \frac{1}{T} - \sum_i (\mathbf{I}_i \nabla) \frac{\mu_i}{T} - \sum_s \theta_s \frac{A_s}{T} + \frac{1}{T} (\mathbf{j}\mathbf{E}), \quad (8)$$

where $A_s = \sum_i \nu_{is} m_i \mu_i \equiv \sum_i \nu_{is} M_i$ is the chemical affinity. We shall find it convenient later to use the Planck functions $\bar{\mu}_i = \mu_i/T$ and $\bar{A}_s = A_s/T$. By introducing the electrochemical potential,

$$\mu_i^* = \mu_i + z_i \varphi,$$

where z_i is the charge of K_i per unit of mass, as well as the generalized heat flux $\mathbf{q}^* = \mathbf{q} + \mathbf{j}\varphi$, we are able to reduce (8) to a form with no explicit electrical term:

$$\rho \frac{\partial s}{\partial t} + \operatorname{div} \frac{1}{T} \left(\mathbf{q} - \sum_i \mu_i \mathbf{I}_i \right) = (\mathbf{q}^* \nabla) \frac{1}{T} - \sum_i (\mathbf{I}_i \nabla) \bar{\mu}_i^* - \sum_s \theta_s \bar{A}_s. \quad (9)$$

Then

$$\mathbf{q}^* - \sum_i \mu_i^* \mathbf{I}_i = \mathbf{q} - \sum_i \mu_i \mathbf{I}_i$$

and by virtue of the conservation law of the electric charge for reactions of the form

$$\sum_i \nu_{is} m_i z_i \equiv \sum_i \nu_{is} Z_i = 0$$

one has $\bar{A}_s^* = A_s$.

It can be shown that the modified Gibbs relation (4) under the assumption (2) of mechanical equilibrium in a field of conservative forces such as in (5) is given by

$$dg^* = -sdT + \sum_i \mu_i^* dc_i,$$

where g is the internal thermodynamic specific potential. The generalized Gibbs-Duhem relation is written as

$$sdT + \sum_i c_i d\mu_i^* = 0.$$

Finally, one also has the relation

$$h^* \nabla \frac{1}{T} = \sum_i c_i \nabla \bar{\mu}_i^*,$$

which enables one to rewrite (9) in the form [2]

$$\rho \frac{\partial s}{\partial t} + \operatorname{div} \frac{1}{T} \left(\mathbf{q} - \sum_i \mu_i \mathbf{I}_i \right) = - \sum_i (\mathbf{K}_i \nabla) \bar{\mu}_i^* - \sum_s \theta_s \bar{A}_s, \quad (10)$$

$$\text{where } \mathbf{K}_i^* = \mathbf{I}_i - c_i \mathbf{q}^*/h^*, h^*$$

this being the generalized enthalpy.

As regards Eqs. (9) and (10), it should be noticed that they remain invariant with respect to the reference levels of φ and h^* . In particular, one can always define h^* such that this quantity remains positive for any $T > 0$.

Equation (10) is identical with its corresponding equation in [2] in the case of the introduced generalized μ_i and \mathbf{K}_i . If, from now on, the asterisk * is omitted, one obtains for s the expression [2]

$$\sigma = - \sum_i (\mathbf{K}_i \nabla) \bar{\mu}_i - \sum_s \theta_s \bar{A}_s, \quad (11)$$

the latter implying the general kinetic equations of the thermodynamics of irreversible processes,

$$\theta_s = - \sum_t L_{st} \bar{A}_t; \quad (12)$$

$$\mathbf{K}_i = - \sum_j M_{ij} \nabla \bar{\mu}_j, \quad (13)$$

where $L_{st} = L_{ts}$ and $M_{ij} = M_{ji}$ are kinetic coefficients. The lack of correlation between the scalar and the vector quantities in (12) and (13) is a consequence of the Curie principle. It appears that in this case there is also an additional reduction of correlation in Eqs. (13).

Let the system under consideration consist of a different kinds of atoms A_l ($l, m = 1, \dots, a$). By the definition of independent reactions one has $a = k - r$. One now orders \mathbf{K}_i in such a way that the first a places are occupied by A_l and the remaining by the molecules $K_{a+s} = \sum_l n_{l,a+s} A_l$, where $n_{l,a+s}$ is the number of A_l in K_{a+s} . If one regards the recombination reactions as independent, one can rewrite (1) as

$$\rho = \frac{\partial c_l}{\partial t} + \text{div } \mathbf{I}_l = - \sum_s m_l n_{l,a+s} \theta_s; \quad (14)$$

$$\rho \frac{\partial c_{a+s}}{\partial t} + \text{div } \mathbf{I}_{a+s} - m_{a+s} \theta_s. \quad (15)$$

The combination of (14) and (15) yields instead of (14) the equations

$$\rho \frac{\partial c_l^0}{\partial t} + \text{div } \mathbf{I}_l^0 = 0, \quad (16)$$

where

$$c_l^0 = c_l + \sum_s \frac{n_{l,a+s} m_l}{m_{a+s}} c_{a+s}; \quad (17)$$

$$\mathbf{I}_l^0 = \mathbf{I}_l + \sum_s \frac{n_{l,a+s} m_l}{m_{a+s}} \mathbf{I}_{a+s}.$$

Thus, the continuity equations (16) for any numbers of atoms in a system take the form of standard equations with no chemical terms. By proceeding now to \mathbf{K}_i^0 in (11) similarly as in (17) one obtains

$$\sigma = - \sum_l (\mathbf{k}_l^0 \nabla) \bar{M}_l - \sum_s (\mathbf{k}_{a+s} \nabla) \bar{A}_s - \sum_s \theta_s \bar{A}_s, \quad (18)$$

where $\mathbf{k}_i = \mathbf{K}_i / m_i$. The kinetic equations which follow from (18) are generally of the form of (12) and (13), that is, in particular,

$$\mathbf{k}_l^0 = - \sum_m M_{lm} \nabla \bar{M}_m - \sum_s M_{ls} \nabla \bar{A}_s, \quad (19)$$

$$\mathbf{k}_{a+s} = - \sum_l M_{sl} \nabla \bar{M}_l - \sum_t M_{st} \nabla \bar{A}_t.$$

The variables in (18) and (19) are now subjected to some linear transformations so that the expression (18) and Eqs. (15) and (16) remain invariant. These transformations are of the form

$$\begin{aligned} \bar{A}_s &= \sum_t a_{st} A'_t, \\ \theta_s &= \sum_t b_{st} \theta'_t, \quad \mathbf{k}_{a+s} = \sum_t b_{st} \mathbf{k}'_{a+t}, \\ \bar{M}_l &= \sum_m c_{lm} \bar{M}'_m, \quad \mathbf{k}_l^0 = \sum_m d_{lm} \mathbf{k}'_m, \end{aligned} \quad (20)$$

where

$$\sum_s a_{s't} b_{s't} = \delta_{st}, \quad \sum_l c_{l'l} d_{l'm} = \delta_{lm},$$

and δ_{st} and δ_{lm} are Kronecker's symbols. Therefore, the unknown quantities in (20) are the r^2 values a_{st} and the a^2 values c_{lm} . Substituting the expressions (20) in (18) and (19), one obtains

$$\begin{aligned} \sigma &= - \sum_l (\mathbf{k}_l^{0'} \nabla) \bar{M}_l' - \sum_s (\mathbf{k}_{a+s} \nabla) \bar{A}_s' - \sum_s \theta_s' \bar{A}_s'; \\ \mathbf{k}_l^{0'} &= - \sum_m M_{lm}' \nabla \bar{M}_m' - \sum_s M_{ls}' \nabla \bar{A}_s'; \\ \mathbf{k}_{a+s} &= - \sum_l M_{sl}' \nabla \bar{M}_l' - \sum_t M_{st}' \nabla \bar{A}_t', \end{aligned}$$

where

$$\begin{aligned} M_{lm}' &= \sum_{l',m'} M_{l'm'} c_{l'l} c_{m'm}; \\ M_{ls}' &= \sum_{m,t} M_{mt} a_{ts} c_{ml} = M_{sl}' = \sum_{m,t} M_{tm} a_{ts} c_{ml}; \\ M_{st}' &= \sum_{s',t'} M_{s't'} a_{s's} a_{t't}. \end{aligned}$$

One can always select the values a_{st} and c_{lm} in such a way that the ar conditions $M_{ls}' = M_{sl}' = 0$ are satisfied. Thus, one can be certain that there is no correlation in the kinetic equations (19) between the group of chemical terms $\bar{A}_s, \mathbf{k}_{a+s}$ and the group $\bar{M}_l, \mathbf{k}_l^0$.

In the stationary one-dimensional case one finds from (3), (5), and (7) that

$$\mathbf{j} = \text{const}, \quad \mathbf{q}^* = \mathbf{q} + \mathbf{j}\varphi = \text{const},$$

and from (16) that $\mathbf{I}_l^0 = \text{const}$; thus in the linear approximation $\mathbf{k}_l^0 = \text{const}$ and the transformed equations (15) are of the form

$$dk_{a+s}/dx = \vartheta_s. \quad (21)$$

By virtue of (12) and (19) the system of equations (21) is closed for the Planck functions \bar{A}_s and can be written as

$$\frac{d}{dx} \sum_t M_{st} \frac{d}{dx} \bar{A}_t = \sum_t L_{st} \bar{A}_t. \quad (22)$$

For $L_{st}, M_{st} = \text{const}$ the solutions of (22) are of the form

$$\bar{A}_s = \sum_t (C_{st}^+ e^{\lambda_t x} + C_{st}^- e^{-\lambda_t x}),$$

where the r values of λ_t are found by solving the secular equation

$$|M_{st} \lambda^2 - L_{st}| = 0,$$

and out of $2r^2$ integration constants C_{st}^\pm only $2r$ are independent and the remaining ones can be expressed in their terms by using (22). Employing the obtained solutions one can express z in terms of φ and solve the last equation of (6).

The actual choice of independent reactions is quite arbitrary, the nonvanishing of the cross coefficients L_{st} ($s \neq t$) is to be understood as taking into account the possible dependent reactions which are not considered explicitly within the framework of the thermodynamics of irreversible processes.

Moreover, the employment of the Planck functions \bar{M}_l and \bar{A}_s as variables permits a natural extension of the analysis just carried out to the case of anisothermic systems with different temperatures of different K_l .

The difference between this study and a similar investigation in [2] lies in that in [2] the matrices $\|L_{st}\|$ and $\|M_{ij}\|$ are diagonalized and one proceeds to formal variables whose meaning is not quite clear whereas in the present work the analysis is carried out in physical variables (in Planck functions \bar{M}_l and \bar{A}_s) which enables us to draw conclusions as regards the specific autonomy of chemical processes. In the general case all kinetic coefficients depend on T and on concentrations: thus a complete separation of the original system of equations is not possible.

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