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Review

Frameworks of separation theories from two separate worlds: dynamics and thermodynamics

Heng Liang^{a,*}, Bing-Cheng Lin^b

^a*Department of Applied Chemistry, College of Chemical Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

^b*Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116012, China*

Abstract

Contemporary separation theories are based on the mass conservation equation with the methods of dynamics, lose the entropy balance equation as a restriction condition, and draw very little from non-equilibrium thermodynamics, cybernetics, information theory and systematology. Thus, they cannot account for the irreversibility of separation processes. In natural sciences, the entropy balance equation is an exclusive way to reveal the evolution that separation systems undergo in order to make solute systems evolve from Boltzmann's disorder to order. The irreversibility of separation processes, which is caused by thermodynamic forces, and described by the entropy balance equation only, is the source of both the separation and mixing of solute systems. Therefore, Clausius' heat death (band spreading of one component) and Darwin's evolutionism (separation among different components) simultaneously coexist in separation processes. The framework of non-equilibrium thermodynamic separation theory is made up of three parts. First, the integral optimization function is found on the part of the mixed entropy change of the solute system between the final state and the initial one relating directly to the net separation. It corresponds to the information quantity that solute systems gain from separation systems. The more negative the integral optimization function is, the more information solute systems gain and the better the integral separation efficiency of big separation systems is. Second, according to the entropy balance equation and the conditions of practical separation processes, a separation state function can be discovered to show how separation systems described by macroscopic physicochemical parameters affect the integral optimization function. Lastly, with the methods of modern cybernetics, we will be able to optimize and time-varyingly control separation processes through controlling the operation parameters in separation processes with the separation state function. The non-equilibrium thermodynamic separation theory will keep separation theories up to date with modern physics and intersecting sciences. © 1998 Elsevier Science B.V. All rights reserved.

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*Corresponding author.

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1. Introduction

Alvin Toffler stressed in the foreword to *Order Out of Chaos* written by Prigogine and Stengers [1], “One of the most highly developed skills in contemporary western civilization is dissection: the split-up of problems into their smallest possible components. We are good at it. So good, we often forget to put the pieces back together again.” Could it be said that this is the case in separation science?

In the present information era, cybernetics, information theory and systematology (named intersecting sciences) are used so widely and so profoundly that tremendous transformations have been made in many fields, such as philosophy, astronautics, engineering, biology, physics and chemistry, economics, political science, etc., in which the concept of entropy is at the center [2–5]. But there are unconquerable obstacles to introducing the principle of intersecting sciences to the framework of contemporary separation theories. The essential reason is that contemporary separation theories, which have drawn very little from these intersecting sciences, are based on the mass conservation equation of a one-component system with the methods of dynamics [6,7]. However, separation processes are certainly irreversible and the solute systems are open systems (in each small volume cell) in thermodynamics [8,9]. Thus non-equilibrium thermodynamics that fully reflects the idea of systematicism can be adopted to describe separation processes and to establish the function relations between various operation parameters and separation efficiency [8–12]. With the non-equilibrium thermodynamic separation model [8,9], the principles of modern cybernetics can be used to properly optimize and time-varyingly control separation processes integrally.

This review tries to trace the physical characters of the mass conservation equation, on which almost all

contemporary separation theories depend and their methods of dynamics. We will reveal the conflicts between contemporary separation theories and related contemporary physics and intersecting sciences. Based on preceding analyses, the framework of non-equilibrium thermodynamic separation theory will be presented to suit the developments of contemporary physics and intersecting sciences.

2. The framework of contemporary separation theories and its limitations

The framework of contemporary separation theories was mainly composed of three brilliant contributions relating to each other, which are based on dynamics with the assumption of thermodynamic equilibrium. In 1940 Wilson originally described the processes of liquid-phase column chromatography based on mass conservation with the supposition of thermodynamic equilibrium and no band spreading [13]. In 1941, Martin and Synge originated ‘theoretical plates’ to indicate column efficiency with the analogy between distillation or extraction and chromatography [14]. In 1956 Van Deemter et al. developed rate theory to relate the band spreading of one component with some operation parameters, such as flow velocity [15]. Up to that time, the basic framework of contemporary separation theories had been roughly formed. The continuity of sciences themselves made the theoretical framework last more than half of a century without any change [6,7]. Giddings [7,16] did a lot of pre-eminent work to enrich this theoretical system. Dondi and Guiochon edited a book on the theories of linear and non-linear chromatography with the methods of dynamics [6]. Hjertén [17] and Grushka [18] used this theoretical framework in capillary electrophoresis. Other separation scientists have done a lot of outstanding works in the many fields of separation science. For exam-

ple, stochastic theories [7,19,20] and their computer simulations [21] in the framework of contemporary separation theories were developed to assist us in understanding separation processes of chromatography and electrophoresis. This theoretical framework started from the conservation equations of mass [13,15], which hold water only for one component, such as Eq. (1), which was used as an essential equation in dealing with linear or non-linear and ideal or non-ideal chromatographs [22]:

$$\frac{\partial C_k}{\partial t} + P \cdot \frac{\partial C_{s,k}}{\partial t} + u \cdot \frac{\partial C_{s,k}}{\partial z} = D_{a,k} \cdot \frac{\partial^2 C_k}{\partial z^2}$$

with $k = 1, 2, \dots, n$ (1)

where t is separation time; z the distance along the transport or separation path; C_k and $C_{s,k}$ the concentrations of solute k in the mobile and the stationary phase, respectively; P the phase ratio; u the mobile phase linear velocity; and $D_{a,k}$ the coefficient of axial dispersion.

We wish to stress here, that Eq. (1) always keeps the character for dealing with the migration and dispersion of one-component only, even though Eq. (1) was extended to the case of a multi-component mixture by the competitive or multi-component isotherms [22]. Actually, competitive isotherms consider only the effect that the concentrations of other solutes have on the distribution of one-solute, and it is impossible to alter the character of the mass conservation law in any process (reversible or irreversible) for one-component. At this point, the mass conservation equation and entropy balance equation do not have any homologous characters, because of the no-conservation character of entropy in irreversible processes [23]. In addition, the mass conservation equation with altered formats was also used as an essential equation in dealing with electrophoresis processes or other separation processes [7,18]. In a word, altering its format cannot change the essential characters of the mass conservation equation.

Under the initial and boundary conditions of the problems studied, the theoretical plate height only relates the band spreading of one-component to its causes (including the concentrations of other components, if multi-component isotherms were considered [22]). Moreover, the contribution of solute-

relative migrations to separation efficiency is associated with the band spreading by the resolution (R_s) [24] or other analogous parameters, such as resolution product, peak capacity [7] or chromatographic resolution statistic (CRS) [25], etc. The quality of the part or entire separation is generally assessed by means of the above functions, which are generally used as objective functions to optimize separations. This theoretical framework has been guiding and promoting the development of separation science in the recent decades and continues to play an important role. The achievement of this theoretic framework in the history of separation science was as resplendent as that of the classical dynamics in the history of nature sciences.

However, separation processes may be examined from another perspective. Firstly, plate theory was established on the basis of the mass conservation continuity equation, the main goal of which is to deal with the diffusion of one-component (also including the contribution of other components). As far as this equation itself is concerned, its solution under the corresponding initial and boundary conditions cannot give the relations between integral separation efficiency and operation parameters, but only gives the distribution of one-component. From the fact that plate theory deals with one-component only, the theoretical framework does not involve the separation between different solutes at all. In fact, plate theory reflects one aspect of separations (i.e. solute zone broadening) only, although the plate height really is closely related with the separation efficiency. Secondly, on the basis of the diffusion equation of one-component systems (plate theory), separation scientists have to deal with the factors of the two sides as two relatively independent subjects, which respectively impel the separating (relative migration of solute bands) and the mixing (the band spreading) in a parataxis station. Thus contemporary separation theories have not found the inherently essential relations of the two opposite and related sides, and cannot form an integral prospect of separation theories either. Thus the optimization of separation efficiency with plate theory can only be considered as a partial optimization method rather than an integral one. Thirdly, using R_s or other analogous parameters as the criterion of separation efficiency has intuitionistic characteristics. However,

they have some insufficiencies. For example, under the same R_s , changing the quantity of the injection sample can result in a difference of separation efficiency. At this point, R_s is quantitative in appearance, but qualitative in essence, because R_s is not directly related to the quantity of the injection sample [9,10,12]. Besides, it is difficult to establish the function relation between various operation parameters and the integral separation efficiency by using R_s , because R_s was introduced into separation science only according to simply apparent measures, and it innately lacks meaning in physics [24]. Lastly, we have found that the irreversibility of separation processes, (which is caused by thermodynamic forces, and described by the entropy balance equation only in non-equilibrium thermodynamics), is the source of both separating and mixing of solute systems [8,9,26,27]. But, the irreversibility in separation processes has not been considered fully in the framework of contemporary separation theories.

In equilibrium thermodynamics, scientists always relate the irreversibility to destructive action only [1]. Based on this viewpoint, plate theory only related the band spreading of a single component to its causes and lacked the entropy balance equation as a restriction condition. It is obvious that Clausius' heat death [1] is essential in forming the framework of contemporary separation theories. In addition, the integral optimization function [9,12], which can not only precisely reflect the separation efficiency of solute systems, but also can optimize integrally various operation parameters based on physical essence, would be absent in the framework of contemporary separation theories. Thus with contemporary separation theory framework, it is certainly difficult to integrally optimize and control the big separation systems which are composed of the separation systems and solute systems. It would be impossible to expect the contemporary separation theories formed in the middle of this century to absorb the idea of non-equilibrium thermodynamics and intersecting sciences. Because during that period, non-equilibrium thermodynamics and intersecting sciences were being initially developed also, and it was impossible for these subjects to filter into the framework of separation theories at that time.

A new theoretical framework of separation science would be needed to assemble the factors of the two sides in one unified form [9,26], where it is won-

drously important to re-understand the role of the irreversibility in separation processes [26,27]. Otherwise it would be difficult to integrally optimize and control separation processes with the methods of modern cybernetics.

3. Transferring our attention from mass to information

Which one among the three elementary physical quantities of natural science should be concerned mostly in forming the inner shell of separation theories, mass, energy or information? Why is it necessary to transfer our attention from mass to information in the transforming of physics and intersecting sciences? In fact, the answers to the two questions are very similar to Schrodinger's idea to stress the significance of the negative entropy, instead of mass or energy, in maintaining life (e.g. keeping order) [28].

Two universal things coexisting in physics, heat and force, are antithetic in competing, and in turn are uniform in making systematic evolution. Thermodynamics challenged dynamics in focusing on the irreversibility of processes. Entropy law, which relates to irreversible processes, has already exceeded the category of conservation laws. The irreversibility prescribes the arrow of time to indicate the evolution in the isolated system, which is always in the direction of making a system more disordered [1]. After the irreversibility of processes was admitted, Darwin's evolutionism and Clausius' heat death theory seem to be opposite, but they are unified on the intrinsic randomness of complex systems. Only in the open system, is it possible for the environment to put the negative flow of entropy into the system to make it more ordered. Simultaneously, the system undergoes irreversible processes to make the entropy production more than zero. Boltzmann's order principle makes the low entropy relate to order and the high to disorder, which associates the entropy and Boltzmann's probability distribution [29]. This graceful breakthrough of Boltzmann was a milestone in leading to the physics of processes.

In equilibrium thermodynamics, the irreversibility always relates to these phenomena, such as friction, viscosity and heat, which explains the reason for energy dissipation. The phenomena were considered

to act destructively only, and caused only by our experimental ability and the lack of subjective ideal control [1]. Of course, contemporary separation theories could not get away from the governing of these basic viewpoints, which were reflected in the opinions of ‘ideal processes of chromatography’ [13,30] and plate theory concerned with the band spreading of one-component only [6,7].

Non-equilibrium thermodynamics [23,31] extended classical thermodynamics to open systems and treated the state parameters of thermodynamics as field variables, that is, as continuous space- and time-dependent fields such as total mass density $\rho(r,t)$, entropy $s(r,t)$ or temperature $T(r,t)$ etc. with the assumption of the local equilibrium. To describe the evolution of many-body systems, the balance equation of entropy plays a central role in near equilibrium. Let us consider a system consisting of n components in a viscous medium without chemical reactions. For a volume cell, by inserting the conservation equations of mass, energy and motion to the Gibbs relation, a general format of entropy balance equation can be obtained [31]:

$$\rho \cdot \frac{ds}{dt} = -\operatorname{div} J_s + \sigma \quad (2)$$

where,

$$J_s = \frac{1}{T} \cdot \left(J_q - \sum_{k=1}^n \mu_k J_k \right) \quad (3)$$

$$\begin{aligned} \sigma = & -\frac{1}{T^2} \cdot J_q \operatorname{grad} T - \frac{1}{T} \sum_{k=1}^n \left(T \operatorname{grad} \frac{\mu_k}{T} - F_k \right) \\ & - \frac{1}{T} \cdot \Pi \operatorname{grad} v \end{aligned} \quad (4)$$

where ρ is the local total density; s the local entropy per unit mass; J_s , J_q and J_k the entropy flow, the heat flow and the diffusion flow of substance k per unit area and unit time, respectively; σ the entropy production per unit volume and unit time; T the local absolute temperature; μ_k the chemical potential of component k ; F_k the force per unit mass exerted on component k ; Π viscous pressure tensor and v the centre of mass velocity.

The first and second terms at the right-hand side of Eq. (2) are respectively, the divergence of a entropy flux and a source term, entropy production. Eq. (3) shows that for open systems, the entropy flow consists of two parts: one is the ‘reduced’ heat flow,

the other is connected with the diffusion flows of matter. Eq. (4) demonstrates that the entropy production contains three different contributions. The first term at the right-hand side of Eq. (4) arises from heat conduction, the second from diffusion, and the third is connected to gradients of velocity field, giving rise to viscous flow. The structure of the expression for σ is that of a bilinear form: it consists of the sum of products of two factors:

$$\sigma = \sum_i Y_i X_i \geq 0 \quad (5)$$

where the Y_i are the thermodynamic fluxes (J_q , J_k , Π etc.), which are ‘driven’ by X_i , the conjugate thermodynamic forces ($-(1/T^2) \operatorname{grad} T$, $-\operatorname{grad} (\mu_k/T)$, $\operatorname{grad} v$ etc.).

In the entropy balance equation, on one hand, entropy production is always a non-negative quantity relating the various irreversible processes occurring in a system. On the other hand, entropy flows, which supply the system with the entropy through its surroundings can be positive, zero and negative. In linear non-equilibrium thermodynamics, the thermodynamic forces are the source of both entropy production and entropy flow [23,26,31]. In other words, the thermodynamic forces are the source of causing the evolution of complex systems (towards order or disorder). The Brussels school originated the view of ‘nonequilibrium may be a source of order’ through analyzing the separation of a mixture of two different gases by applying a thermal gradient to the system [29]. In fact, the separation of isotopes by thermal diffusion was a typical separation technology at the beginning of separation science [32].

Further, we noted that one thermodynamic force always causes two opposite kinds of effects simultaneously. One is in entropy flow, and this could put negative entropy flows into object systems to make the system more ordered through matter and energy or informational exchange, and this effect incarnates the idea of Darwin’s evolutionism [26]. The other one is in entropy production, which always increases the entropy of object systems to make the system more disordered, and this effect incarnates the idea of Clausius’ heat death of the universe. Thus the thermodynamic forces in lineal non-equilibrium thermodynamics have more profound meanings than that in Newtonian mechanics. Newtonian forces that indicate the reciprocity between two monomers are

only presented in the first grade law introduced by Eddington [33]. Moreover, thermodynamic forces reflect the effect of outside surroundings to the molecule aggregation of the inside of object systems, and directly indicate the irreversible behavior in the evolution of object systems, which are presented in the second grade law introduced by Eddington [33].

Boltzmann's order principle clarified that the nature of diffusion phenomena is that energy is distributed in multi-energy levels, and the degree of order is not related to the energy directly, but to the energy distribution [29]. Obviously, the entropy concept reveals that the system evolves from disorder to order in near equilibrium region, and indicates the limitations of the framework of contemporary separation theories with the mass and energy conservation laws by the methods of dynamics.

Separation process control is more important than describing or understanding them. Of course, we ought to adopt the concepts and methods of cybernetics, system and information theory to control separation processes.

In 1945 Schrodinger noted the significance of the 'negative entropy' to life [28]. In 1948 Wiener discovered the relationship between entropy and information in founding cybernetics [34]. In 1949 Shannon founded information theory and used the formula to measure information, which is the same as the measurement entropy used by Boltzmann [4]. In 1950 Brillouin systematically demonstrated and developed the thought that information is equated to negative entropy (flow). In other words, gain in entropy always means loss of information and nothing more [5]. After noting the equivalence relationship between information and negative entropy, now we can begin to answer the question, how do we control separation processes to gain more information (or negative entropy) through separation systems? Before answering this question, we need a deeper understanding of the irreversibility of separation processes.

4. Irreversibility in separation processes

Irreversibility (the arrow of time) is known by not only most scientists, but also by many of the populace [35]. It is demonstrated by the second law

of thermodynamics and is true in any reality process. Are separation processes reversible or irreversible at all? Essentially, no separation has been accomplished in equilibrium states and reversible processes, and non-equilibrium in the neighborhood of equilibrium could not be the basis to assume that the processes of chromatography or electrophoreses are always reversible processes or in thermodynamic equilibrium states. The irreversibility of separation processes can be explained from a few aspects. (1) The actualizing of any separation process necessarily depends on the applied fields (e.g. chemical potential, electrical, sedimentation and temperature graduations, etc.) provided by separation systems. In fact, the fields are irreversible surroundings for solute systems [7]. (2) In the applied fields, the different kinds of solute molecule aggregation (solute band) could be separated on the separation pathway. Thus the solute systems are provided with negative entropy flow (negentropy) by separation systems (as surroundings), which makes the solute system evolve from disorder to order and obtain information [9,11]. This was shown in Eq. (3). (3) Just for the sake of separating, the irreversible processes caused by the applied fields are adopted in any separation. It follows that irreversible processes accompany entropy production with no-negative values, which correspond to the factors making solute zone spreading and information loses. Obviously, both separation among bands and spreading of bands originate from the irreversibility simultaneously [26].

Why has non-equilibrium thermodynamics not been adopted as the framework of separation theories up to now? There are possibly a number of causes, such as horrendous complexity of non-equilibrium thermodynamics (especially for separation scientists, who always and must focus on the experiments), the premature estimation of the cost/benefit of this research or the lack of funds and lack of political interests in separations, etc. However, the above causes are probably not essential. In fact, the main reason is a clash of doctrines between dynamics and thermodynamics [1,29,36].

The conflict between dynamics and thermodynamics focuses on the second law of thermodynamics, because the second law cannot be deduced from the framework of classical dynamics. The conflict in physics has been actively discussed since

1865, when Clausius introduced the concept of entropy (S). Boltzmann's famous equation, $S = k \log P$, relates entropy to probability: entropy grows because probability grows. Eddington [33] considered that "the law that entropy always increases, the second law of the thermodynamics, holds, I think, the supreme position among the laws of nature . . ." Planck [37] wrote, "It would be absurd to assume that the validity of the second law depends in any way on the skill of the physicists or chemist in observing or experimenting. The gist of the second law has nothing to do with experiment: the law asserts briefly that there exists in nature a quantity, which changes always in the same sense in all natural processes." But some scientists did not agree with the viewpoints, they considered the second law is the result of approximations, the intrusion of subjective view into the exact world of physics. For example, Born stated [1], "Irreversibility is the effect of the introduction of ignorance into the basic laws of physics."

Prigogine and Stengers [1] have given a deeper understanding of the second law. They found three basic elements in the description of irreversibility: Intrinsic irreversibility \rightarrow intrinsic randomness \rightarrow instability. But intrinsic irreversibility is the strongest property: it implies randomness and instability. No general derivation of irreversibility from dynamics is to be expected, because irreversibility is not a universal property. For intrinsic random systems, the concept of probability acquires a dynamical meaning. In the transition from an intrinsic random system to irreversible system, two Markov chains can be obtained, which respectively point to two opposite time orientations (past and future), which correspond to two dynamic realities respectively. The Markov chain corresponding to the reality in natural world would be given only when the second law of thermodynamics is taken as a selection principle. Thus, far from destroying the formidable structure of dynamics, the second law adds an essential new element to it [1,36]. Now it is easy to understand why the separation scientists standing on dynamics did not desire to deal with separation processes with non-equilibrium thermodynamics.

In stochastic approaches, the diffusion equation (mass equilibrium continuity equation in separation science, for example, Eq. (1)) is a special case of the

Markov process. Obviously, the diffusion processes have intrinsic randomness, and they can stochastically evolve along two Markov chains oriented in opposite time directions (future and past). Here, each Markov chain involves symmetry-breaking, which corresponds to one realization of dynamics. When the second law is considered as a selection principle, intrinsically random systems can be transmitted to intrinsically irreversible systems. Thus we can just find the true description of actual diffusion processes with the second law.

Now we have understood why the second law is absolutely necessary in describing the diffusion processes of one component at essentially a physical level. However, solute systems have a number of different molecules in the order of the magnitude of Avogadro's number, thus solute systems are complex systems in physics undoubtedly [38]. Separation processes involve two different diffusions having respectively two opposite contributions to separation efficiency in the applied fields: one is the band spreading of one component, another is the separation among the bands of different components. Therefore, separations among components were only achieved in non-equilibrium states and irreversible processes. And the irreversibility of separation processes has to be described by the entropy balance equation instead of the second law. If the methods of dynamics are only used to deal with separation processes, irreversibility in separation processes as a restriction condition (the entropy balance equation) is lost, which leads to difficulty in establishing the relationship between operation parameters and separation efficiency quantitatively and systematically.

5. Co-existence of Clausius's heat death and Darwin's evolutionism in separation processes

Do separation processes belong to Clausius's heat death or to Darwin's evolutionism or both? In actual separation processes we found not only Clausius's heat death for the inevitable band spreading (more disorder), but also Darwin's evolutionism for the separating among bands (more order). How do the two opposite sides actually unify in the separation processes?

At present, there are no other choices at all.

Non-equilibrium thermodynamics describes the evolutionary behaviors of complex systems with state parameters. From the viewpoint of non-equilibrium thermodynamics, we can find that separations are processes in which different solutes evolve from disorder to order in applied fields (separation among different components) and simultaneously each solute itself evolves from order to disorder (band spreading of one component). The two opposite processes originate simultaneously from the irreversibility of separation processes, which are described quantitatively by the items of entropy flows and entropy production, respectively. In separation processes, a portion of negentropy flow is used up by entropy productions. Thus, the results of separation processes (the degree is the order of solute systems) are determined by both the negentropy flows and entropy productions. Obviously, the entropy balance equation adequately incarnates the dual nature of the irreversibility through the opposite contributions of the constructive action of negentropy flows and the destructive action of entropy productions. In the entropy balance equation, thermodynamic forces, X_i are thermodynamic variables, and the thermodynamic fluxes, Y_i are kinetic variables [39]. Thus, all terms of Eq. (2) have dual characters of dynamics and thermodynamics, and the two terms at the right-hand side of Eq. (2) indicate the entropy changes of the solute system determined respectively by Darwin's evolutionism (entropy flow) and Clausius' heat death (entropy produce).

6. The framework of non-equilibrium thermodynamic separation theory

In the framework of non-equilibrium thermodynamic separation theory, the solute systems consist of two or more components. If only a one-component system is chosen (plate theory), the separation is not involved principally. A separation system means the whole separation surroundings contribute to the separation of the solute system except the solute system itself. So we also name the separation system as the environment of the solute system. It is in correspondence with the concepts of the system and environment in thermodynamics [23,31]. The assemblages of the separation systems

and solute systems compose the big separation systems, whose various properties and interactions can be described by using certain macroscopic physicochemical parameters. The essence of the integral optimization is just the optimization of the big separation system.

6.1. Non-equilibrium thermodynamic essence of separations

Separation processes, which are related to distribution, diffusion, electrokinetic effects and heat transports etc, typically belong to the category of linear non-equilibrium thermodynamics [23,31]. Giddings has pointed that separation processes are irreversible or, more descriptively, one way only. But he did not follow it far. Valentin presented the theory of zonoids with a new geometric approach to remove some of the limitations of contemporary separation theories. He pointed out that entropy production is the root of the mixing process in the separation process [6]. However his theory did not exceed the framework of plate theory [6,7,14]. Non-equilibrium thermodynamics had not been introduced fully into separation science before we pointed out that non-equilibrium may be a source of separations [8,11], on the basis of which we presented a non-equilibrium thermodynamic separation model in capillary electrophoresis [9].

The physical essence of separations is making the solute system so it does not restore to an equilibrium state by applying outside forces, therefore solute systems in separation processes are always in a series of non-equilibrium states in the neighborhood of equilibrium. This physical behavior is stable and the responses of the solute systems to any changes of initial and boundary conditions and its surroundings (separation system) can be predicted. Thus we can indicate separation efficiency with the mixed entropy change related directly to net separation processes [9,12].

6.2. Integral optimizing function of separation efficiency (ΔS_s)

The integral optimizing function of separation efficiency is based on the idea of the black box theory in systematology. For any separation pro-

cesses, we always provide mixed samples in which there are two or more components with different moles, after separating, we want to know how many moles of the components have separated. Here we do not care what separation methods are used and how separation processes are carried out. Of course, the optimizing function must easily relate operation parameters to the integral separation efficiency, too.

Giddings described the dissipative (band broadening) roles of entropy, and emphasized that entropy is the single greatest enemy of separations because of its universal inclination to dilute and remix components that have been so carefully isolated in space [40]. De Clerk and Cloete adopted specific entropy to indicate the extent of separation [41]. Stewart studied the entropy measurement and evaluation of separation qualitatively [42]. With Grand Canonical Ensemble we found the function relationship between the entropy of solute systems and solute distributions [43], and that the kinetic energy distribution of solute molecules is the common essence of the entropy and density distribution of solute zones, and the entropy, entropy change and the rate of entropy change of a solute system are a group of characteristic functions to indicate separation efficiency [44].

However, we found that two bottlenecks prevent the entropy concept from being developed into

separation science fully and quantitatively. First, the net separation entropy change, which is only associated with net separation processes, has not been differentiated from the total mixed entropy change of the solute system in total separation processes. Second, the total mixed entropy change of the solute system is not related to operation parameters (macroscopic physicochemical processes) with the entropy balance equation. Thus it is just as Giddings thought “While the formalism of irreversible thermodynamics provides an elegant framework for describing molecular displacements, it provides too little substance and too much conceptual difficulty to justify its development here.” [7]

We can divide the whole separation process into the following successive processes in Fig. 1, (1) The process of net volume change of the solute system from V_0 to V_1 , in which no separation of solutes is involved, corresponds to the mixed entropy change ΔS_1 ; (2) The process of net separation of the solute system, in which the total volume keeps constant while the individual volume of each solute changes from V_1 to V_{1i} or V_{1j} , corresponding to the mixed entropy change ΔS_2 ; (3) The process of net distribution change from the even distribution to arbitrary distribution (separation results), in which the volume of each solute zone and the total volume of the solute system keep constant, corresponds to the

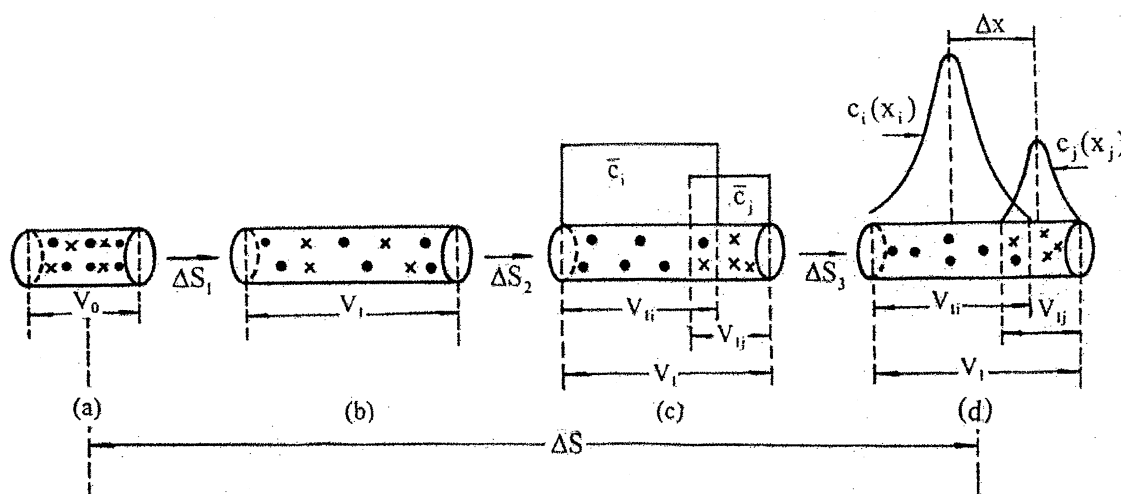


Fig. 1. The spreading and separating of the two-component system in successive processes. They are, respectively, the processes of net volume changing from (a) to (b), the net separation from (b) to (c), and the net distribution changing from (c) to (d). The mixed entropy changes of each process and the whole process are ΔS_1 , ΔS_2 , ΔS_3 and ΔS , respectively.

mixed entropy change ΔS_3 . Clearly, we can get the total entropy of the solute system (ΔS) [9,12],

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 \quad (6)$$

Here ΔS does not correspond to the integral separation efficiency of the big separation system. Therefore we must find a new function, the integral optimizing function of separation efficiency (ΔS_s), based on the concept of the mixing entropy of the solute system. It can be calculated directly from the distributions and relative positions of solute zones and the number of moles of solutes to indicate separation efficiency integrally and quantitatively for any arbitrary distribution of solute zones [12],

$$\begin{aligned} \Delta S_s = \Delta S_2 - AR \int_{x_{i,1}}^{x_{j,1}} c_i(x) \ln [c_i(x)/\bar{c}_i] dx \\ - AR \int_{x_{i,2}}^{x_{j,2}} c_j(x) \ln [c_j(x)/\bar{c}_j] dx \end{aligned} \quad (7)$$

where

$$\Delta S_2 = n_i R \ln (V_{1i}/V_1) + n_j R \ln (V_{1j}/V_1) \quad (8)$$

where, suppose a solute system is made up of two components i and j with n_i and n_j moles, as shown in Fig. 1. V_0 is the common volume that components i and j occupy in the initial state. V_1 , V_{1i} and V_{1j} denote the total volume and the individual volumes that two components i and j occupy in the final state, respectively. A is the cross-sectional area perpendicular to the separation path. R the gas constant. x the coordinate along the separation path. $x_{i,1}$, $x_{i,2}$, $x_{j,1}$, $x_{j,2}$ are respectively, the boundaries of separated component i and j ; \bar{c}_i and \bar{c}_j are the average concentrations of component i and j in the separation path.

We also obtain ΔS_s from Eq. (6) to relate to the total entropy of the solute system (ΔS),

$$\begin{aligned} \Delta S_s = \Delta S - \Delta S_1 \\ + AR \int_{x_{i,2}}^{x_{j,2}} \{c_i(x) \ln [c_i(x)/\bar{c}_i] \\ + c_j(x) \ln [c_j(x)/\bar{c}_j]\} dx \end{aligned} \quad (9)$$

where

$$\Delta S_1 = (n_i + n_j)R \ln (V_1/V_0) \quad (11)$$

Physically, ΔS_s is equal to the amount of information that the solute system gains from its separation surroundings, or separation system. It is quantitatively related to the irreversibility of separation processes, and corresponds to the extent of Boltzmann order. In separation science, ΔS_s corresponds to the quantity of separated solute [12].

6.3. Separation state function on the entropy balance equation

It is necessary to establish a state function to time-varyingly control operation parameters in order to suit the demand of modern cybernetics [45]. Of course, we must understand how separation systems affect the information quantity of solute systems (the integral separation efficiency) through the exchanges of mass, energy or information between solute systems and their surroundings (separation systems). The function relationship between the integral optimizing function and various operation parameters can be developed mainly by the entropy balance equation. With this function relationship, we can integrally optimize the various operation parameters, and time-varyingly control a few of the operation parameters to realize the integral optimal separation.

Onsager's reciprocal relations affirmed that thermodynamics could provide available information in the neighborhood of equilibrium. The direct value of the combination of the entropy production and Onsager's reciprocal relations resulted in the description of linear non-equilibrium thermodynamics. The set of conservation laws (mass, energy and momentum), entropy balance equation, the equations of state and phenomenological equations may be said to be complete, which may be solved under the proper initial and boundary conditions for a material [1,31].

The entropy balance equation, (Eq. (2)) is only available for small volume cells, which are so small that the thermodynamic properties of the system vary little over each cell but large enough for the cell to be treated as macroscopic thermodynamic subsystems in contact with their surroundings. Therefore, we cannot only define thermodynamic

variables and functions in the cells, but also wish to vary them from cell to cell in such a way that the thermodynamic variables can be described in continuous space and time-dependent fields [46]. Thus solute systems in a cell form an open system of thermodynamics, because the exchange of heat and matter between the cell and its surrounding can be found in Eqs. (2) and (3).

From Eqs. (2)–(4), we can get the total entropy of the solute system:

$$\begin{aligned} d_e S &= - \int_0^t dt \int_{\Omega} J_{s,\text{tot}} d\Omega \\ &= - \int_0^t dt \int_{\Omega} (J_s - \rho sv) d\Omega \end{aligned} \quad (12)$$

$$d_i S = \int_0^t \int_V \sigma dV \quad (13)$$

where $d_e S$ is the entropy supplied to the solute system by its surroundings; $d_i S$ the entropy produced inside the solute system; V the volume that the solute system occupies; and Ω the boundary of the volume. $d_i S$ is zero for reversible processes and positive for irreversible processes.

With Eqs. (12) and (13), we can obtain the total entropy of the solute system in the whole separation processes:

$$\Delta S = d_e S + d_i S \quad (8')$$

Now by inserting Eqs. (3) and (4) into Eqs. (12)–(14) to develop Eq. (9), we can obtain a separation state function to discover the relationship between the integral optimization function and the operation parameters.

In practice, many fields (the gradients of chemical potential, external fields and temperature) [7] used to promote separations unexceptionally result in both effects: entropy flux and entropy production, which are related deeply to each other in the entropy balance equation. The entropy flux corresponds to the relative migration of the mass center of different solutes partly due to the differences of solutes themselves, e.g. electric charge, mass, size, shape, hydrophobicity and affinity, etc., partly due to the

properties of the mobile phase and stationary phase or applied fields. Here, we stress the matching between the characters of solutes and applied fields (including mobile phase and stationary phase), and we can describe them suitably in the diffusion flow of substance k , J_k and heat flow, J_q in Eqs. (2) and (3). Separation scientists have known well the gradient of temperature due to Joule heating in CE [47], and also noted the influence of adsorption heat on elution band profiles in nonlinear liquid chromatography [48]. Diffusion flow and heat flow always coexist [49] in electroseparation methods, which are related to electrophoreses, electroosmosis or electroendosmosis and partition etc. Increasing relative migration among solutes and releasing more heat from solute systems imply that separation systems put more negentropy flow into solute systems. In this aspect, all separation conditions as the separation surroundings are equivalent to Maxwell's Demon [4] in that they supply the solute system with negative entropy flow and make the solute system more ordered (better separation efficiency). The entropy production is the entropy production inside solute systems related to the irreversible processes, which contain three contributions due to heat conduction, diffusion and viscous flow in general separation processes, which correspond to related factors contributing to band spreading. From the above analysis, in practice, we would develop the entropy balance equation of solute systems into the separation state function in many separation methods.

With the entropy balance equation, the equations of state and phenomenological equations and a group of conservation laws (mass, energy and momentum), the separation state function could be obtained between the integral separation efficiency and operation parameters to describe the big separation system. The more negative ΔS_s ($\Delta S_s < 0$) is, the more information solute systems gain and the better the separation efficiency is [9,12]. It is obvious that, effective separation systems can supply solute systems with more negentropy, which was called the amount of information by Wiener [4]. The amount of information in separations corresponds to the quantity of separated solutes, which is incarnated in the number of separated peaks and their quantity (namely the number of separated solute moles).

A non-equilibrium thermodynamic separation

model has been proposed in capillary electrophoresis (CE) [9]. This model considers the separation processes as the two opposite sides in unity: the separating among solute bands and the band broadening synchronously in one theory framework. The former corresponds to the entropy flow and the latter to the entropy production of solute systems in linear non-equilibrium thermodynamics. The separation state equation between separation efficiency and various operation parameters was found in CE.

7. Separation process control with the methods of modern cybernetics

The entropy flux and the entropy production of solute systems are indiscernible integration in comprehensively describing the evolution of the systems in the separation state function. If one focuses only on the factors making band spreading with theoretical plates or rates theory, it is part optimizing. If one focuses on the factors of the two opposites yet unifying them, it is integral optimizing. That the part optimizing cannot replace the integral optimizing is a basic principle in system theory [50,51]. In a word, non-equilibrium thermodynamic separation theory can be used to control the operation parameters of big separation systems in order to supply solute systems with more negentropy flow, simultaneously making the solute systems produce lesser entropy productions. It is our final aim to obtain the most negative of the integral optimization function, which corresponds to the integral optimization of the big separation systems.

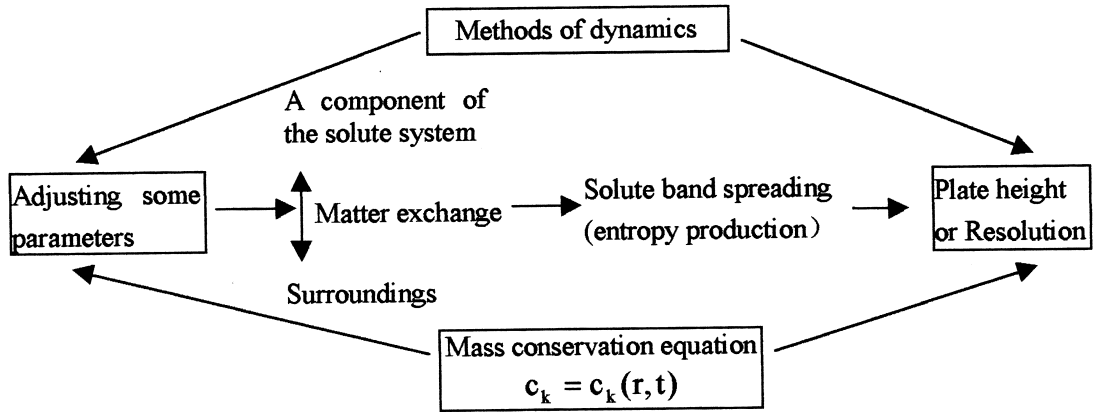
However, the separation state function of any practical big separation system would be horrendously complex. Fortunately, at this time computers run speed high enough to favorably perform the operation of the separation state function in practical separation processes. Cybernetics and system theory also offer effective and powerful arithmetics with compact formats to solve the state equation [45]. Of course, we must re-organize the separation state function by using methods of modern cybernetics and system theory [50,51]. In addition, network thermodynamics [52] is an important tool to make the separation state function suit the demand of modern cybernetics on topology and geometric graph

theory. One of the functions of non-equilibrium thermodynamic separation theory would provide the optimized and time-varying constraints of various parameters in separation processes to make the black box, we assumed, transfer to a white box (a gray box at some time) in separation science.

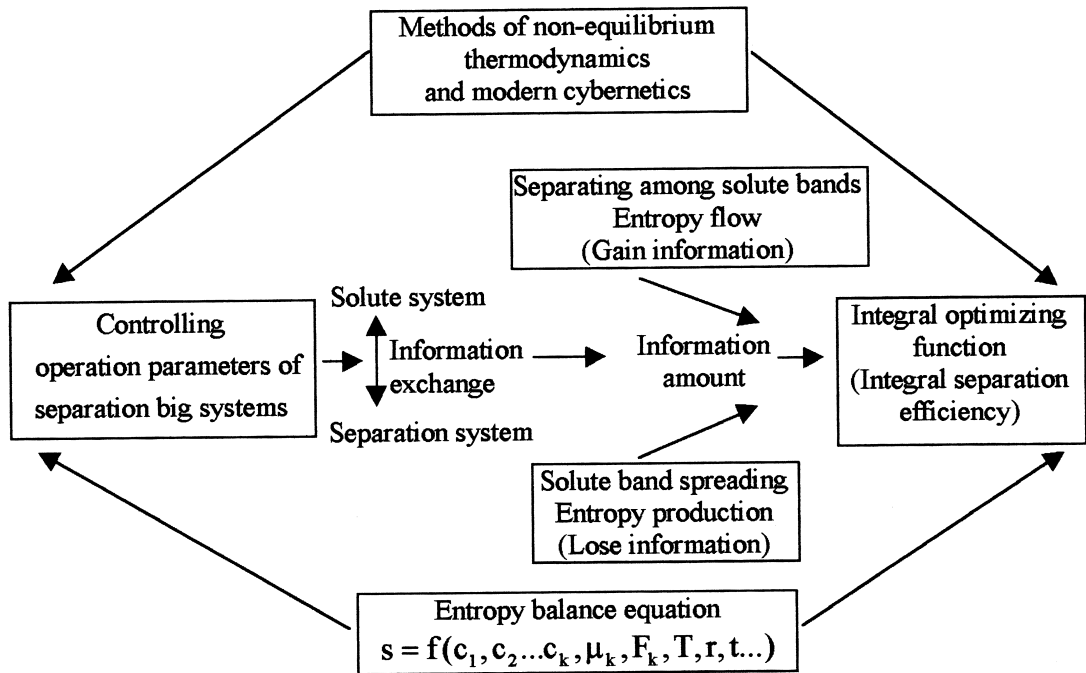
8. Re-putting contemporary separation theories together on non-equilibrium thermodynamics

Dynamics and thermodynamics are two complementary explanations of nature, which can be unified by a noncanonical transformation. We must abandon the usual formulation of dynamics to reach the thermodynamic description [1,29,36]. In the framework of non-equilibrium thermodynamic separation theory, we only insert a new element, the irreversibility of separation processes, into the framework of contemporary separation theories. Thus there is no conflict in any levels between contemporary separation theories and non-equilibrium thermodynamic separation theory, where the former specializes in dealing with the details of separation processes and the latter acts as an integral framework for whole separation processes. In non-equilibrium thermodynamics, the entropy balance equation contains three kinds of (mass, energy and momentum) conservation equations with no conflict, in which the mass conservation equation only deals with each component in the solute systems [31]. Obviously, we can use all achievements of contemporary separation theories on conservation equations to enrich non-equilibrium thermodynamic separation theory with no conflict. Thus non-equilibrium thermodynamic separation theory cannot replace contemporary separation theories. Fig. 2 shows the frameworks of contemporary separation theories and non-equilibrium thermodynamic separation theory.

In conclusion, non-equilibrium thermodynamic separation theory emphasizes the two opposite actions of the irreversibility in separation processes. Thermodynamic forces make solute bands not only spread but also separate. Integral optimization means that the opposite actions of thermodynamic forces must be considered in one theoretical framework. Non-equilibrium thermodynamic separation theory can be used to integrally optimize and time-varyingly



A. The framework of contemporary separation theories.



B. The framework of non-equilibrium thermodynamic separation theory

Fig. 2. The frameworks of contemporary separation theories (A) and non-equilibrium thermodynamic separation theory (B). Where c_k = the local density of component k ; r = space vectors; t = time; s = the local entropy of solute system per unit volume; μ_k = chemical potential of component k ; F_k = external force per unit mass acting on component k .

control separation processes with the methods of modern cybernetics. When non-equilibrium thermodynamic separation theory puts contemporary separation theories back together again, separation science will achieve the unification between art and science on the basic levels of natural science.

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