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A Classification Framework for Separation Science

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Summary

A general framework for the development of separation science is proposed which links the criterion of merit via an effective transport equation to the molecular basis of separation processes.

There are numerous indications in the literature (e.g., *1–3*) that separation science is beginning to evolve as a separate discipline. In such a new field which derives its origin from a variety of sources, some initial amount of confusion, especially in the definition of objectives, can be expected. The purpose of the present paper is to suggest a possible scheme by means of which separation processes can be classified and which can serve as a logical conceptual framework for the general development of the subject.

It is necessary, at the outset, to distinguish clearly between what will be called macroscopic and molecular separation processes. Molecular separations involve the separation of individual molecules while macroscopic separations denote processes in which the entities being separated are macroscopic aggregates of molecules. (Molecules are here used as a collective term to include ions and atoms.) This distinction is convenient since separations exploit the differences between the component entities; on a molecular scale these can be reduced to a limited number of molecular properties while a different set would apply on a macroscopic scale. Although the present systematization is primarily concerned with molecular separations, it will be evident that a parallel scheme can be formulated for macroscopic separations.

THE MOLECULAR BASIS

The state of molecules is completely determined by its state function ψ which is the solution of the complete Schrödinger equation for the given collection of nuclei and electrons. This function is usually written as the product $\psi = \psi_n\psi_e$ by invoking the Born–Oppenheimer approximation where ψ_n is a function only of nuclear and ψ_e only of electronic parameters. The functional dependence of each of these functions can be symbolically written as

$$\psi_e = \psi_e\{(x_e, t)m_e, q_e\}$$

and

$$\psi_n = \psi_n\{(x_n, t)m_n, q_n\}$$

where the subscripts e and n refer to electrons and nucleons, respectively. The group (x, t) represents the independent position and time variables for the description of the mechanical motions of the particles; the parameters m and q denote their masses and charges, respectively. As far as we know at present, this set of variables and parameters provides an adequate basis for a description of molecular phenomena. The molecular parameters, i.e., parameters that reflect the collective motions of the fundamental component particles of a molecule, can be classified in terms of a statistical model of the molecule. Since quantum mechanics postulates that $\psi^*\psi$ gives the probability distribution (for normalized ψ) in the configuration space spanned by the coordinates of all the component particles, the description can conveniently be reduced to a consideration of the various moments of the suitable probability distributions in ordinary three-dimensional space. This may, in principle, be effected by means of standard statistical mechanical procedures (*4*). The two fundamental parameters are m and q, so that the obviously important distributions are those for mass and charge.

The mass probability distribution $\rho_m(\mathbf{r})$ will consist mainly of a number of sharp peaks centered on the various nuclei as a result of the very high nuclear mass density relative to the electronic mass density. The total information contained in ρ_m is far too detailed for direct incorporation into separation theories, and the art will be to abstract that which is necessary. One expects that size and shape will be important parameters, and quantitative measures for this purpose may be formulated by defining various statistical moments.

(a) The zeroth moment

$$\mu_{m0} = \int_V \rho_m d\mathbf{r} = m \tag{1}$$

where $d\mathbf{r}$ is a volume element in the three-dimensional space, is merely equal to the total mass of the molecule.

(b) The first moment

$$\boldsymbol{\mu}_m = \int_V \frac{\mathbf{r}\rho d\mathbf{r}}{m} \tag{2}$$

is a vector which gives the position of the center of mass of the molecule relative to the chosen origin.

(c) The second moment

$$\mu_{m2} = \int_V \frac{(\mathbf{r} - \boldsymbol{\mu}_m)\cdot(\mathbf{r} - \boldsymbol{\mu}_m)\rho d\mathbf{r}}{m} \tag{3}$$

is a scalar which gives a measure of the size of the molecule in terms of the radius of an equivalent sphere. The center of this sphere coincides with the center of mass. More information about the shape may be formulated by means of the second moments in the coordinate directions, e.g.

$$\mu_{m2x} = \int \frac{\{(\mathbf{r} - \boldsymbol{\mu}_m)\cdot\mathbf{i}\}^2 \rho dr}{m}$$

(d) The three components of the vector defined by the third moment

$$\boldsymbol{\mu}_{m3} = \int_V \frac{(\mathbf{r} - \boldsymbol{\mu}_m)(\mathbf{r} - \boldsymbol{\mu}_m)\cdot(\mathbf{r} - \boldsymbol{\mu}_m)\rho dr}{m} \tag{4}$$

defines the asymmetrical distortion of the equivalent sphere in the directions of the coordinate axes to approximate more closely the actual shape of the molecule.

One can therefore conclude that the zeroth moment gives the exact mass while the second and third moments provide rough but well-defined measures for the size and shape of the nuclear skeleton of the molecule. The fact that the μ_m refer to the nuclear framework of the molecule and not to the molecule itself is important since the electronic charge density contours need not follow the contours of the mass density distribution. For although the electronic distribution is of extremely low density relative to the mass density of the nuclei themselves, it is highly incompressible as a result of the Pauli exclusion principle.

THE CHARGE DISTRIBUTION

Similar considerations to that employed in the mass distribution apply in the case of the charge distribution. However, a matter of more importance here is the interpretation of intermolecular forces in terms of ρ_q. These may be classified in terms of the range of the interaction. As the intermolecular distance decreases, a succession of attractive and finally repulsive forces become operative. The longest range potentials are related to the zeroth moment of ρ_q and is known as the monopole potential. These fall off as R^{-1} while the dipole term, which derives from the first moment, is proportional to R^{-2}. The dispersion interaction is of paramount importance since it is always present between molecules and, being proportional to R^{-6}, is of such short range that it depends on the sizes and shapes of the interacting molecules (*5*).

The molecular charge distribution is in reality generated by electronic currents which give rise to magnetic fields. These may also be described in terms of moment theory but, since the resulting forces are relatively weak, the role that they play in molecular separations is minor. (They can become important in cooperative phenomena but these belong to macroscopic separations.)

Acceleration of the charge distribution, corresponding to transitions between energy states in quantum theory, gives rise to the absorption or emission of radiation and differences in this respect may be utilized in an indirect way for separation purposes.

A facet of all these interactions of particular significance for separation processes is the possibility of regarding the interaction as consisting of two mechanisms, action and reaction; interaction between molecules A and B is thus interpreted in terms of the effect of A of a potential field due to B and vice versa. If interaction can be decoupled in such a way that the interaction between arbitrary pairs of molecules may be expressed in terms of parameters inherent to the individual molecules, the whole framework would be immensely simplified. This is especially important in dispersion interaction, and the formulation of semiempirical combination rules can be expected to receive considerable attention within the context of separation science.

In summary, one can say that the molecular properties of primary importance for purposes of separation can be classified under the main headings of (a) mass and (b) interaction differences. The first is well-defined both theoretically and experimentally but much remains to be done in the elucidation of intermolecular forces. The repulsive forces are primarily responsible for the sizes and shapes of molecules, and in this respect the moments of the distributions may prove to be of value. The attractive forces are dependent on a number of parameters, e.g., size, shape, and polarizability, and an adequate set of basis parameters, in terms of which effective intermolecular potentials which are dependable yet simple enough for incorporation into the framework of separation science can be formulated, is still lacking at the present time.

THE CONCENTRATION DISTRIBUTION

The actual separation of the molecules takes place on a macroscopic scale and consists of (a) an input, (b) a separation process, and (c) an output consisting of the separated components. This output may always be represented as a spatial concentration distribution $C(\mathbf{r})$, but since separations are also time-dependent, the way in which t is eliminated calls for some consideration. For the sake of simplicity, a single separation coordinate, z, will be considered here. Let C_{i0} denote the concentration of the ith component in the original mixture, the state of which is referred to by the subscript zero. The aim of a separation process can now be defined as the creation of new states in such a way that the concentration C_{ij} of component i in a state j will at some later time have increased to a prescribed level in excess of the concentrations of the other components from which it is to be separated. States are here used in the sense of the general definition of a partition state as proposed by Rony (*11*). Regions created by fraction cutting is therefore included in the definition. Let $C_{ij}(z, t)$ be the concentration distribution of the ith component in the jth state. This concentration distribution may now, for instance, be moving past a fixed sensor at a constant velocity u_z so that C_{ij} is recorded as a function of time. However, this may easily be converted to a distance coordinate z' by multiplying the time scale by u_z. The $C_{ij}(z')$ which results is then the appropriate distribution for a fraction cutter located at the sensor. [This $C_{ij}(z')$ is actually not identical to the actual distance distribution due to the finite time which the sample takes to move past the detector, but this is usually not a large effect.] Such separations in which $(\partial C_{ij}/\partial t) \neq 0$ at the time and position of the cut point will be termed dynamic separations. If, on the other hand, $(\partial C_{ij}/\partial t) = 0$ under the same conditions, the process will be termed static. The important observation is that the output from the separator can always be expressed as a concentration distribution in a distance coordinate which will here be denoted by z. This applies to all separation processes, irrespective of the number of states involved in the actual process itself. However, the equations used in predicting $C(z)$ will differ according to the time scale on which the separating mechanism functions. If one ignores quantum phenomena, the finest scale will be that on which significant time intervals are smaller than the time between molecular collisions, and classical mechanics will have to be used. For larger time intervals, statistical averages become appropriate and eventually one ends up with the macroscopic equations of change known as the transport equations. These are by far the most important for separations, particularly in multistate systems, and merits further discussion.

The central equation for separation is obviously that describing mass transport. For each component in every state there are but three mechanisms by means of which the concentration can change, viz., convection, diffusion, and transfer to or from some other state. These processes are mathematically described by the three terms on the right-hand side of Eq. (5) (D_{ij} assumed constant).

$$(\partial C_{ij}/\partial t) = -\nabla \cdot u_{ij}C_{ij} + D_{ij}\nabla^2 C_{ij} + Q_{ij} \tag{5}$$

If there are n components and k states, one therefore starts out with a set of $n \times k$ simultaneous partial differential equations. The first assumption which is usually made is that these may be uncoupled with respect to the components so that each component can be solved for separately. Such a coupling may be due both to chemical reaction or physical interaction between the components. The problem is thereby effectively reduced to the solution of k equations where the coupling between the k states is effected via the Q_j-terms. These terms may, to the first order, be described by means of equations of the form

$$Q_j = \sum_l \Lambda_{lj}C_l - \Lambda_{jl}C_j \tag{6}$$

known as "master equations" (*6*). The Λ_{ij} are conditional transition probabilities per unit time and part of the program of separation science will be their formulation in terms of molecular properties, thereby linking the macroscopic theory to the molecular world.

In the actual solution of the equations, resort usually has to be taken to approximation procedures, either in the modeling or the mathematics or both, and various methods have been explored. Giddings (*7*) reviews those which culminated in his generalized nonequilibrium theory of chromatographic processes. Significant advances are also recorded in the engineering sciences (e.g., *8–10*). In particular, the method of moments analysis by Laplace transform techniques appears very promising and could very well become a standard method for the description of linear systems.

This method involves the calculation of the statistical moments of the concentration distribution in a state *j*. The procedure involves in the first place the conversion of the set of partial differential equations to a set of ordinary differential equations in which the time variable has been eliminated. This is done by Laplace transforms. This system is then solved by reducing it via the coupling terms to a single differential equation, the solution of which in turn yields expressions for the moments through the relation (*15*)

$$\mu_k = (-1)^k \lim_{s\to 0} \left(\frac{\partial^k \tilde{c}_{ij}}{\partial S^k}\right) \Big/ \lim_{s\to 0} \tilde{c}_{ij} \tag{7}$$

These moments are defined relative to the distribution in time, but if the effect of the finite time taken to move past the detector can be taken into account, the moments relative to the distribution in *z* may be computed.

A knowledge of these moments now makes possible the formulation of an effective mass transport equation for component *i* in the *j*th region, viz.

$$\frac{\partial C_{ij}}{\partial t} = \Lambda_{ij}{}^e C_{ij} - u_{ij}{}^e \frac{\partial C_{ij}}{\partial z} + D_{ij}{}^e \frac{\partial^2 C_{ij}}{\partial z^2} - S_{ij}{}^e \frac{d^3 C_{ij}}{\partial z^3} \tag{8}$$

The Λ^e represents the effect of chemical reaction on the zeroth moment, or total mass *m* of the component *i* while the other coefficients are related to the higher moments by:

$$d\mu_1/dt = u_{ij}^e \quad \text{where} \quad \langle z \rangle = \mu_1 = \int_{-\infty}^{+\infty} \frac{zC_{ij}\,dz}{m}$$

$$d\mu_2/dt = 2D_{ij}^e \quad \text{where} \quad \mu_2 = \int_{-\infty}^{+\infty} \frac{(z - \langle z \rangle)^2 C_{ij} dz}{m}$$

$$d\mu_3/dt = 6S_{ij}^e \quad \text{where} \quad \mu_3 = \int_{-\infty}^{+\infty} \frac{(z - \langle z \rangle)^3 C_{ij} dz}{m} \qquad (9)$$

Actually, the moments technique has not been employed to eliminate the other coordinates of the *j*th state orthogonal to *z*. These correspond to the so-called mobile phase terms in chromatographic theory and is at present most satisfactorily handled by the generalized nonequilibrium theory (*7*). The important phenomena associated with transfer and resistance to mass transfer in other states are adequately described in Eq. (8), provided that transport in these other states can again be effectively reduced to taking place in one dimension.

In order to avoid confusion, the meaning of the effective coefficients in Eq. (8) should be compared to an analogous equation (cf. Eq. 24 in Ref. *11*) used by Rony in his classification scheme for ideal partitioning separation systems. Rony assumes that equilibrium between states is instantaneously attained so that his effective coefficients do not take nonequilibrium effects into account. For classification purposes, this distinction between ideal and nonideal systems is irrelevant and one can use the effective coefficients as the basis for a classification scheme in the same way as Rony did. It is important to note, however, that the present scheme includes, in principle, all types of separation systems and is not restricted merely to multistate partition systems. For instance, in the case of single state systems, it can be expected that the various moments will in some cases be calculated by mechanical equations other than the transport equations. However, even in such cases Eq. (8) can again be used as describing a simulated separator where the various coefficients are now functions of the parameters of the actual separator. The main classification of separation processes according to the effective transport equation then follows as:

(a) Chemical separation due to differences in the Λ_{ij}^e.
(b) Differential migration as a result of differences between u_{ij}^e.

(c) Diffusional separations based on differences between D_{ij}^e for different components i.

Various combinations of these form a secondary classification scheme. Differences between the S_{ij}^e which determine the asymmetry of the distribution can be expected to be of marginal value as a basis for separation; they are more likely to be of importance as detrimental factors.

THE CRITERION OF MERIT

It is important to stress the fact that the effective coefficients that determine the various statistical moments are themselves functions of two distinct types of parameters, viz., (a) those which are related to the system being separated, i.e., "chemical" parameters which are again functions of molecular parameters, and (b) "physical" parameters which are related to the design and operation of the separating system. Indeed, the central aim of separation theory may be formulated as the ability to predict the optimum design and operating variables for the best separation method on being given the set of molecular parameters defining the inherent properties of the constituent molecules of the mixture. The concepts of "optimum variables" and "best separation method" obviously imply a criterion of merit relative to which comparisons can be made. Unfortunately, there is no universal criterion since separations may be made with a variety of priorities in mind. In different applications, one might, for instance, assign different relative weights to the demands required of resolution, speed, and capacity. However, in all separations the primary aim is that the components be adequately separated and a specification to this end is always included in all criteria of merit. A satisfactory measure of the degree of separation is therefore an essential element of separation theory. Rony has demonstrated the versatility of his index of separation in a series of papers (e.g., *1*, *12*, *13*) and the relation of this index to a more general criterion in terms of the entropy of separation has been formulated (*14*).

A basic requirement of a satisfactory separation criterion is that it should be both easily measurable and also be functionally related to the fundamental theoretical description of the separation process in a simple and direct manner. Formulation in terms of the various moments would admirably satisfy both these requirements but the general feasibility of such a procedure has not been explored.

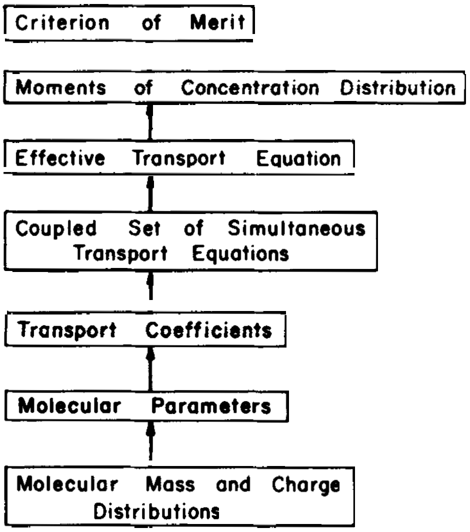

FIG. 1. Framework for separation science.

The future will undoubtedly see the development of very complex criteria of merit. Thus the present practice of ultimately assessing separational processes in terms of financial considerations is bound to undergo changes under the influence of the new trends evident in public opinion.

CONCLUSIONS

The framework for the conceptual development of separation as a science as described above are conveniently summarized in Fig. 1. This diagram illustrates the way in which the criteria of merit are linked via the description of the separation process to the fundamental molecular properties of the components of the mixture. It also emphasizes the primary task of separation theory: the specification of the process variables that will optimize the separation for a given initial molecular configuration.

SYMBOLS

$C(\mathbf{r})$	spatial concentration distribution
$\tilde{c}$	Laplace transformed concentration function

D	diffusion coefficient
$d\mathbf{r}$	differential volume element
Λ_{ij}	conditional transition probability per unit time
m	mass
μ_i	ith moment
ψ	state function
q	charge
Q	source-sink term
$\mathbf{r}$	position vector
R	intermolecular distance
ρ	probability density
s	Laplace transform parameter
S	coefficient defined by Eq. (8)
t	time
u	velocity
x	position coordinate
z	separation coordinate

Superscripts

e	effective

Subscripts

e	electron
i	component
j	state
m	mass
n	nuclei
o	original mixture
q	charge

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