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Entropy as a General Separation Criterion

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Summary

A quantitative measure for the extent of separation, based on the specific entropy, is derived. Two functions are shown to be suitably related to this measure to qualify as resolution functions. The first is Glueckauf's impurity ratio; the second is a new function termed the purity index. The relationship between the latter and Rony's extent of separation is demonstrated.

ENTROPY AS GENERAL SEPARATION CRITERION

In a recent series of papers (e.g., *1–3*) Rony has made a significant contribution to the development of separation science as a distinct discipline. His studies are based on a criterion of merit which was chosen primarily for mathematical convenience. The aim of the present study is to derive, from a physical basis, a quantitative measure for the extent of separation and to demonstrate the relationship of Rony's criterion to this new index.

Entropy of Separation

Separation and purification have become practically synonomous terms so that a separation process can be defined as the separation of a mixture of substances into physically distinct regions, the aim being to alter the composition within a region in such a way as to lower the concentration of one or more components in a specific region to an acceptable level.

The increase in entropy when m substances are mixed is given by (*4*)

$$\Delta S = -R \sum_{i=1}^{m} n_i \ln y_i \tag{1}$$

where intermolecular forces are neglected. n_i is the number of moles of component i and y_i is its mole fraction in the mixture. Equation (1) can be re-written as

$$\Delta S = S_2 - S_1$$

where

$$S_2 = (\sum n_i) \ln (\sum n_i)$$

and

$$S_1 = \sum n_i \ln n_i \tag{2}$$

can be regarded as the entropy of the completely mixed and completely pure states, respectively. The latter may here be regarded as a convenient reference state. For the present purpose, the coefficient R is arbitrary and is conveniently set equal to unity. It will now be shown that this concept may be used to formulate a suitable index for separation. This may be done in a completely abstract manner independent of the separation process used. However, for the sake of clarity, chromatographic separations are here taken as model. Consider, for instance, the chromatogram in Fig. 1. If the fractions were cut at the indicated point and collected separately, the entropy in the jth vessel would be given by

$$S_j = (\sum_i n_{ij}) \ln (\sum_i n_{ij}) \tag{3}$$

where n_{ij} is the number of moles of component i in the jth vessel. We will use the convention that the jth region contains the largest fraction of the jth component. This definition is not complete, however, since the reference state relative to which the entropy is measured has not yet been defined. The definition of such a state is arbitrary but for the purposes of characterizing separation it is convenient to take it relative to the state in which all the components of the jth region have been completely separated. This is illustrated schematically as State A in Fig. 1. The reason for not using State B as reference is also apparent

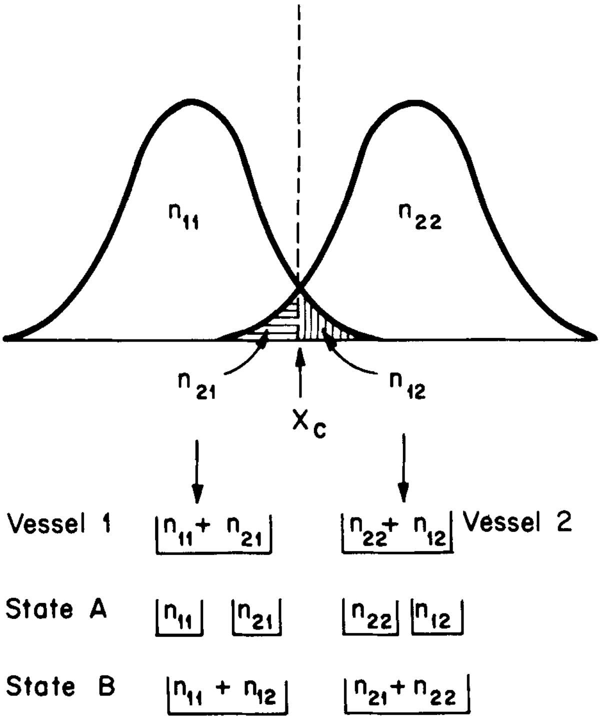

FIG. 1. Illustration of the entropy of separation

from this figure; the extra entropy change in going from A to B is not physically significant in the separation sense. The expression for the total entropy then becomes

$$S = \sum_j S_j \tag{4}$$

where

$$S_j = \left(\sum_i n_{ij}\right) \ln \left(\sum_i n_{ij}\right) - \left(\sum_i n_{ij} \ln n_{ij}\right) \tag{5}$$

In chemical analysis the aim is usually to characterize the extent of separation as such, and to regard the number of moles separated in the process as a separate problem. Since the present analysis is concerned with the former goal, it is convenient to introduce the concept of specific entropy S_j' of a region j. This is defined by the entropy per mole of the region and follows from Eq. (5) as

$$-S_j' = \frac{\sum_i n_{ij} \ln n_{ij}}{\sum_i n_{ij}} - \ln \sum_i n_{ij} \tag{6}$$

with

$$S' = \sum_j S_j' \tag{7}$$

Resolution Functions

The expression for specific entropy given in Eq. (7) may be inconvenient to use in practice due to difficulties in its experimental measurement, mathematical manipulation, or both. To circumvent such difficulties functions can be introduced which are in a 1–1 correspondence with the specific entropy and which exhibit extrema at identical values of the independent variables. Such functions will be termed resolution functions, and will be illustrated here by means of a binary mixture.

For a binary mixture Eq. (7) becomes

$$-S' = \frac{n_{11} \ln n_{11} + n_{21} \ln n_{21}}{n_{11} + n_{21}} - \ln (n_{21} + n_{11}) + \frac{n_{22} \ln n_{22} + n_{12} \ln n_{12}}{n_{22} + n_{12}} - \ln (n_{22} + n_{12}) \tag{8}$$

Equation (8) may be re-written as

$$S' = S_1' + S_2'$$

with

$$-S_1' = \frac{1}{1+\eta_1} \ln \left(\frac{1}{1+\eta_1}\right) + \frac{\eta_1}{1+\eta_1} \ln \left(\frac{\eta_1}{1+\eta_1}\right) \tag{9}$$

and

$$-S_2' = \frac{1}{1+\eta_2} \ln \left(\frac{1}{1+\eta_2}\right) + \frac{\eta_2}{1+\eta_2} \ln \left(\frac{\eta_2}{1+\eta_2}\right) \tag{10}$$

where

$$\eta_1 = n_{21}/n_{11}$$

and

$$\eta_2 = n_{12}/n_{22}$$

are the impurity fractions (*5*) of the respective regions. S_j' is seen to be a function only of the impurity fraction of the jth region. The task in formulating a resolution function for S_j' is therefore to find a suitable function of η_j which is in a 1–1 correspondence with S_j'.

Equation (9) may be simplified by noting that as η_j decreases,

$$S_j' \longrightarrow -\eta_j \ln \eta_j \tag{11}$$

This is an acceptable approximation for $0 < \eta_j < 0.1$ as can be seen from Fig. 2. Equation (11) suggests two suitable resolution functions, viz.

$$M_j = \eta_j \tag{12}$$

and

$$I_j = -\log_{10} \eta_j \tag{13}$$

M_j is merely the impurity ratio as originally suggested by Glueckauf (*5*); I_j will be termed the purity index and, since it has been found to be mathematically particularly convenient, merits further discussion.

The Purity Index

The fact that I_j and S_j' are functionally related does not imply that this also applies to $S' = \sum S_j'$ and $I = \sum I_j$, since a specific value for I is not uniquely related to a value of S'. This does not disqualify I as an index for separation; the relative merits of S' and I depend on their relation to the significant factors involved in the separation. The direct link of S' with thermodynamics promises a more generally applicable role for the specific entropy in separation science; the purity index, on the other hand, is mathematically more convenient. Both I and S' are, however, defined on the same basis, viz., the η_i's, and can be formally put into 1–1 correspondence by considering the quantities defined by setting all the η_i's equal to each other. The present analysis will be restricted to the purity index.

Consider, first, the two-component case. Then

$$\begin{aligned} I &= -\log \eta_1 - \log \eta_2 \\ &= -\log \eta_1\eta_2 \\ &= -\log\,(n_{21}/n_{11})\,(n_{12}/n_{22}) \\ &= -\log\,(n_{21}/n_{11})[(n_1 - n_{11})/n_{22}] \end{aligned} \tag{14}$$

Let n_{21}, n_{22}, and n_1 be held constant. I will then decrease as n_{11} decreases

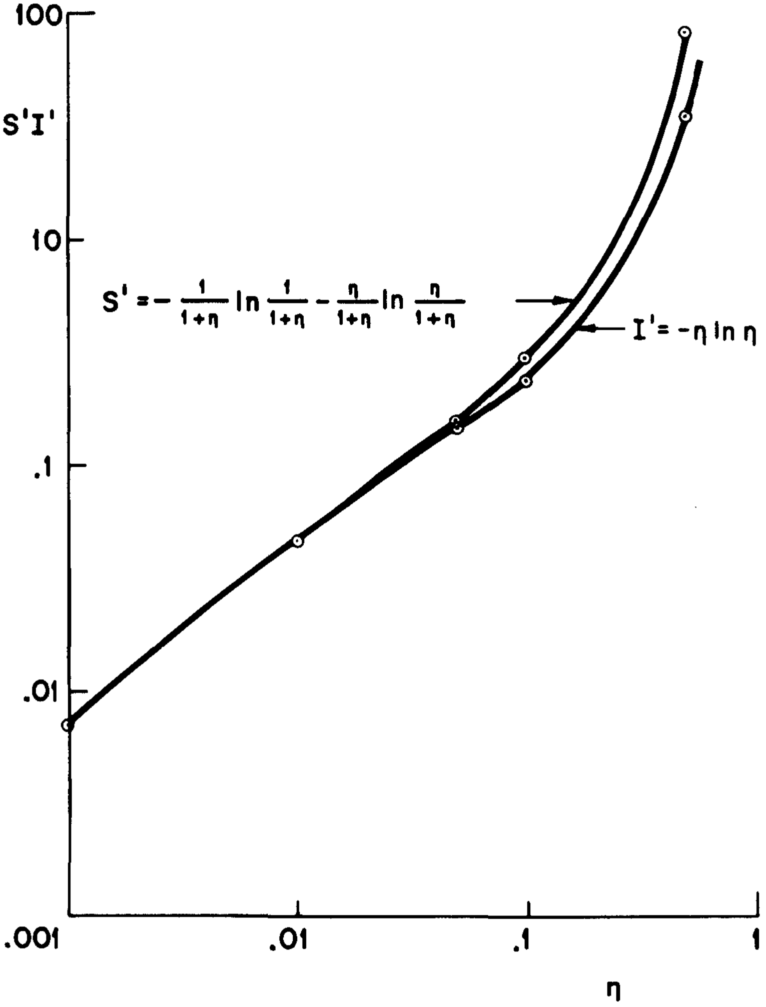

FIG. 2. Comparison of specific entropy S' and the function $-\eta \ln \eta$ as a function of the impurity fraction η.

until $n_{11} = n_1/2$. A further decrease is not possible without a redefinition of the regions. Similarly, the minimum with respect to n_{22} is reached at $n_{22} = n_2/2$. Substitution of these values in Eq. (14) yields

$$I_{\min} = -\log 1 = 0 \qquad (15)$$

This corresponds to maximum impurity. As the separation improves,

I increases. Consider, for example, a cut point defined in such a way as to make $\eta_1 = \eta_2$. The numerical value of I as a function of the impurity is depicted in Fig. 3. If 1% impurity is accepted as a useful norm, it is convenient to define

$$I_2 = -0.25 \log \eta_1\eta_2 \tag{16}$$

where the coefficient 0.25 makes $I_2 = 1$ for 1% impurity of both regions.

The relation between Rony's ξ and the purity index can be clarified by writing I for the binary mixture as

$$\begin{aligned} I &= \log (n_{11}n_{22}/n_{21}n_{12})(n_1n_2/n_1n_2) \\ &= \log (n_{11}n_{22}/n_1n_2) - \log (n_{12}n_{21}/n_1n_2) \end{aligned} \tag{17}$$

The corresponding ξ is given by

$$\xi = \mathrm{abs}[(n_{11}n_{22}/n_1n_2) - (n_{12}n_{21}/n_1n_2)] \tag{18}$$

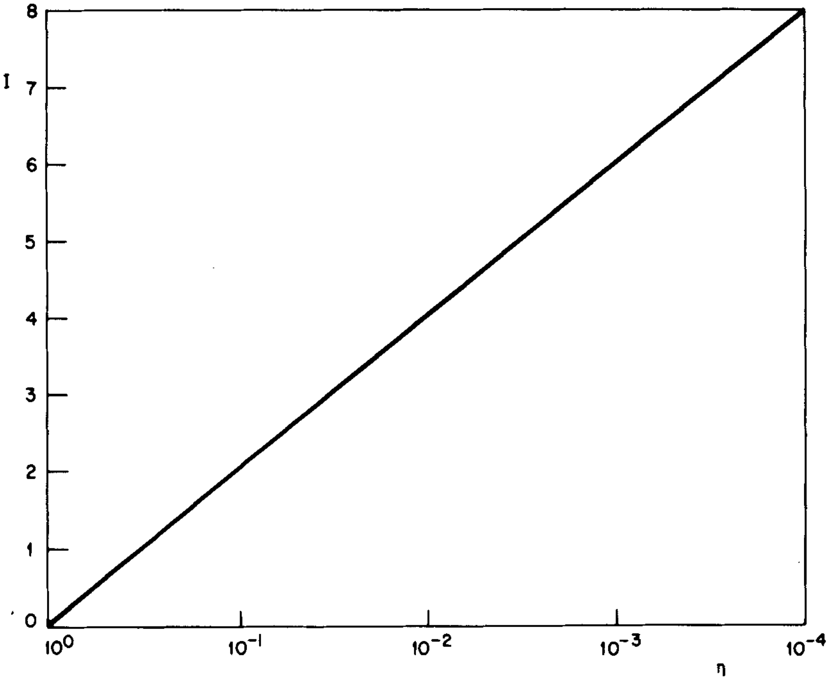

FIG. 3. Purity index I as a function of impurity fraction η for an equimolar two-component mixture with $\eta_1 = \eta_2 = \eta$.

which shows that I is the difference between the logarithms of two quantities whose difference (absolute value) is ξ. The important thing to note is that ξ cannot be written as a function solely of η_1 and η_2, which implies that it cannot be a general measure of the specific entropy. In the limit of close separations, however, ξ is directly related to I_2. For instance, in systems where recovery is made in two distinct phases between which the components distribute, one has

$$\begin{aligned} 2.3I_2 &= -0.25 \ln (n_{21}/n_{11})(n_{12}/n_{22}) \\ &= 0.25 \ln (K_2/K_1) \\ &= 0.25 \ln \alpha \\ &\sim 0.25(\alpha - 1) \qquad \text{for small } \alpha \end{aligned}$$

while

$$\begin{aligned} \xi &= (\text{abs}/n_1n_2)(n_{11}n_{22} - n_{12}n_{21}) \\ &\sim 0.25(\alpha - 1) \qquad \text{when } n_1/2 \sim n_{11} \\ & \qquad\qquad\qquad\qquad\quad n_2/2 \sim n_{22} \end{aligned}$$

which corresponds to close separations. When the division between regions takes place in the same phase, it follows similarly:

$$\begin{aligned} 2.3I_2 &= -0.25 \ln (n_{21}/n_{11})(n_{12}/n_{22}) \\ &\sim 0.25[1 - (n_{21}n_{12}/n_{11}n_{22})] \\ &\sim (n_1n_2)^{-1}(n_{11}n_{22} - n_{21}n_{12}) \qquad \text{for close separations} \end{aligned}$$

i.e., when $n_{11} \sim n_1/2$ and $n_{22} \sim n_2/2$.

The above treatment of binary systems can be extended to multicomponent separations. It then follows from Eq. (7) that the approximate expression for S_j', corresponding to Eq. (11) for the two-component case, is given by

$$S_j' = -\sum_i \eta_{ij} \ln \eta_{ij} \tag{19}$$

where $\eta_{ij} = n_{ij}/n_{jj}$ is the impurity ratio for the ith component in the jth region. For the comparison of separation processes, it will probably only be necessary to consider certain standard binary mixtures, so that Equation (19) will not be further explored here.

In conclusion, the present analysis has demonstrated the potential of the entropy concept as a basic facet of separation science. Of primary importance is the result that it is a function only of the various impurity ratios, thereby relating the practically important purity specification to the basic theory.

SYMBOLS

α	relative volatility
η	impurity fraction
I	purity index
I_2	binary purity index
k	mass distribution coefficient
M	impurity ratio
n	number of moles
R	gas constant
S	entropy
S'	specific entropy defined by Eq. (6)
y	mole fraction
ξ	Rony's extent of separation

Subscripts

i	component
j	region

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REFERENCES

1. P. R. Rony, *Separ. Sci.*, *3*, 239 (1968).
2. P. R. Rony, *Separ. Sci.*, *3*, 425 (1968).
3. P. R. Rony, *Separ. Sci.*, *4*, 447 (1969).
4. K. Denbigh, *The Principles of Chemical Equilibrium*, Cambridge Univ. Press, Cambridge, 1966, p. 118.
5. E. Glueckauf, *Trans. Faraday Soc.*, *51*, 34 (1955).

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