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THE REVERSIBLE AND IRREVERSIBLE SEPARATION OF GASES BY PARTITION CHROMATOGRAPHY

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Abstract. A conceptual, but concise, account of the nature of the partition gas chromatographic separation process, from the view point of thermodynamics and with special reference to entropy changes, is presented. Based on a philosophical and qualitative approach, illustrated through simple physical principles, the treatment embodies the quantitative aspects of the problem as well. This has been taken up with regard to the free energy of dilution, or for that matter, the entropy of mixing and unmixing. Furthermore, the quantitative contributions of the carrier gas and the liquid stationary phases to the overall entropy changes have been derived for a binary system, whereby the analysis reveals the isentropic nature of the chromatographic separation process.

When a mixture of two gases, say 1 and 2, is passed through a chromatographic column, loaded with a suitably chosen stationary phase, the separation of the two gases is achieved in the form of two bands. In an ideal chromatographic column, which operates at a constant pressure and in which the equilibrium between the two phases is instantaneous and other possible irreversible effects such as longitudinal and eddy diffusion are absent, the concentration profile does not change while passing through the column, and each band obtained is of rectangular shape with well-defined sharp rear and front. Although ideal conditions of this type, and hence the rectangularization of concentration profiles, cannot be realized in practical chromatographic columns, the band spreading due to the effect of diffusion at both ends of the band can, however, be neglected provided the band width is much greater than the HETP of the column. The assumption of constant column pressure is equivalent to neglecting the work of separation demanded by the viscous flow, a condition which can be achieved in the limit. Even if the effect of viscous flow in the column were finite, it will have no influence on the separation, because it is the same as would be in the case of carrier gas alone. We observe that after the separation of the components the column is found in its original state, showing that an ideal chromatographic column can separate the two components without any expenditure of work.

The question now arises whether we can interpret the chromatographic separation as a reversal of the diffusion process. If so, then in the light of the second law of thermodynamics, according to which the diffusion process is irreversible, the chromatographic separation of the mixture cannot be achieved, since the reversal of an irreversible cannot be performed without doing any work. Apparently, we are faced with a paradox and should naturally be interested in its solution.

Qualitative Interpretation—A Simple Analogy. Let V be the volume of the sample of two mixed gases. On chromatographic separation, each component occupies a volume of $V_1 = V_2 = V$. If these separated components, kept apart by a partition, were mixed again through a diffusion mechanism by removing the partition, then the volume available to each gas would be V_1+V_2 instead of V_1 and V_2, where $V_1+V_2 = 2V$. On the other hand, if the separated components were fed back into the same column, one after the other, with an appropriate time lag, equal to the time of separation, the components will emerge from the column as a 'mixed band' of volume V, showing once again that the volume of the overlapping gases is the same as the volume of the initial sample of mixed gases. This, in fact, offers the key to the solution of the paradox.

The chromatographic separation is not the reversal of the diffusion process. If it were the reversal, then on mixing the separated components by diffusion, the mixture, as stated above, will have double its original volume.[1] Alternatively, we must first compress the separate gases to one-half of their volume before mixing them together through diffusion to obtain the original volume V of the mixture. Whereas the first stage (compression) is followed by a decrease of entropy, the second stage (diffusional mixing) is accompanied by an equal increase in entropy, so that the overall entropy change remains zero. This obviously leads us to the conclusion that the mixing or unmixing of components by partition chromatography is an isentropic process, which can be achieved reversibly without any expenditure of work.

This reminds us of the use of semipermeable membranes by means of which the irreversible process of diffusion can be performed reversibly. That is to say, that gases can be mixed or unmixed in such a way that the entropy of the system before and after mixing is the sum of the entropies of the separated gases—Gibbs law of partial entropies. It is clear from this that the partition chromatography bears an analogy to the Planck device (a system of gas cylinders fitted with an appropriate semipermeable membrane, placed in vacuum, which can be telescoped into each without friction) which allows reversible, isentropic mixing or unmixing of gases without utilising any work. However, it must be observed that whereas the reversible mixing or separation of gases through the use of ad hoc semipermeable membranes could be a 'thought experiment', the chromatographic separation or mixing

does not suffer from this limitation, but is a practical reality of much wider scope. It is interesting to note that a stationary phase having a retentive power zero for a gas must be conceived as an impermeable membrane for that gas.

Quantitative Thermodynamic Aspects. While resolving the paradox, we concluded rather qualitatively that the chromatographic process is isentropic. The discussion was confined only to the column inlet (just before separation) and the column outlet (just after separation). However, there is a whole gamut of effects which occur even in an ideal chromatographic column right from the inlet to the outlet,[2] such as the involvement of the mobile and the stationary phases and the development (overlapping and separation) of bands of various constituents as they move along the column which are in one way or other associated with entropy changes. Although for any change the thermodynamic functions, such as entropy, are independent of the mechanism, depending entirely on the initial and final stages, it is interesting to apportion the overall entropy change and then see how at any stage of development of chromatographic processes the entropy is conserved.

Consider a component in the form of a plug separated by an imaginary partition from the carrier gas. Now conjecture that the partition is withdrawn, under isothermal and isobaric conditions, allowing spontaneous mixing between the two species, the mixture occupying an extended volume proportional to the column length L. This will certainly produce what is usually (though perhaps inadvisedly) called the entropy of mixing between the two different gases. This gain in entropy is given by:

$$\Delta S_g = -Nk[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)] \qquad (1)$$

where N is the total number of molecules of the mixed population, k is the Boltzmann constant and x_1 the mole fraction of the component mixed with the carrier gas. As we are not interested in the absolute values of the various contributions to the overall entropy change within the column during the chromatographic separation, a more convenient parameter, the reason for the choice of which appears later, will be introduced. Assuming a column of uniform cross-section A, operating at a constant pressure P, the total number of molecules N will be proportional to the column length L. Dropping the proportionality constant AP/kT we may write:

$$\Delta S_g = -L[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)] \qquad (2)$$

As the component is soluble in the stationary phase, we shall have to take into consideration the entropy change in the stationary phase. This entropy change arises from the dilution effect, on account of the greater avidity of the component for the liquid phase. It is effectively equal to the difference between the entropy of the stationary phase of length L in equilibrium with the vapour at mole fraction x_1 in the gas phase and the entropy of the stationary phase of length x_1L in equilibrium with the pure vapour, the total amount of the vapour being the same in the two

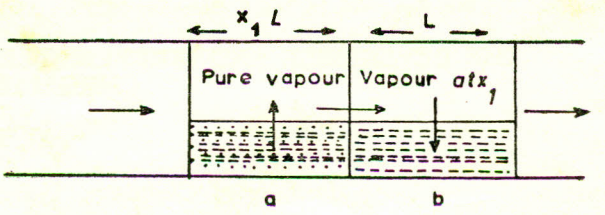

Fig. 1. Entropy change due to (a) the stripping effect of moving phase and (b) the retentivity of stationary phase.

lengths. This can pictorially be visualised as given in Fig. 1. This entropy increase, usually referred to as the entropy of mixing, is essentially due to the lowering of the partial pressures of the two gases which after mixing occupy an increased volume. The free energy of dilution per mole, Δg, from mole fraction unity to x_1 is $\Delta g = RT \ln x_1$. As the vapour in both cases is in equilibrium with the stationary phase, Δg must also give the free energy change in going from the stationary phase of length x_1L to length L. Recalling that $(\delta G/\delta T)_P = -S$, the entropy change per mole will be $-R \ln x_1$. Taking R_1 as the migration factor (not to be confused with the gas constant R as given in above relations), the moles of the vapour in the liquid phase will be proportional to $Lx_1\,(1-R_1)/R_1$, and hence the required entropy change in the same units, ΔS_1, for the stationary liquid phase will be given by:

$$\Delta S_1 = -Lx_1(1-R_1)/R_1 . \ln x_1 \qquad (3)$$

Adding equations (2) and (3), the total contribution to entropy from the gas and the liquid phases, for rectangular shaped bands formed under the ideal conditions, for a single component system extended over a column length L, is given by:

$$\Delta S = -L\left[\frac{1}{R_1}x_1 \ln x_1 + (1-x_1)\ln(1-x_1)\right] \qquad (4)$$

For a multicomponent system, say containing n components, the total entropy change associated with the components and the stationary phase, we may write the generalized expression:

$$\Delta S = -L\left[\sum_{i=1}^{n}\frac{1}{R_i}x_i \ln x_i + (1-\sum_{i=1}^{n}x_i)\ln(1-\sum_{i=1}^{n}x_i)\right] \qquad (5)$$

where $i = 1,2,3,\ldots,n$ and R_i and x_i are the migration factor and the mole fraction of component i respectively.

The Isentropic Nature of Chromatographic Process. To demonstrate the isentropic nature of the chromatographic process, we shall make use of equation (5) for the simple binary system in which only component 1 is retained whereas component 2 travels straight through the column ($R_2 = 1$) alongwith the carrier gas. For this particular system, equation (5) for the total entropy change associated with the unseparated (mixed) components may be written as:

$$\Delta S^m = -L\left[\frac{1}{R_1}x_1 \ln x_1 + x_2 \ln x_2 + (1-x_1-x_2) \ln (1-x_1-x_2)\right] \quad (6)$$

After separation, the band of component 1 will still have the length L, since the unretained component 2 is simply replaced by the carrier gas. On the other hand, component 2 because of its higher concentration will occupy a smaller column length. As the ratio between the molar concentrations of the unretained component and carrier gas will remain constant, the fraction $(x_2/1-x_1-x_2)$ must always have the same magnitude. If x_2 is the mole fraction of component in the mixed state, then at the point of separation from the first component, we should have:

$$\frac{x_2}{1-x_1-x_2} = \frac{x_2^\circ}{1-x_2^\circ}, \text{ giving } \frac{x_2}{x_2^\circ} = 1-x_1 \quad (7)$$

where the superscript (°) designates the state of separation. It is evident from this that if L and L° be the lengths of the unretained component before and after the separation of the first component then $x_2 = x_2^\circ(1-x_1)$ or $x_2^\circ = x_2/(1-x_1)$.

Due to higher concentration the second component must shrink from length L to $L^\circ[=L(1-x_1)]$ to maintain conservation of matter. Now we shall require to calculate the entropy changes for the system when components 1 and 2 are separated from each other. In the case of separated unretained component we need replace L by $(1-x_1)$ L, x_1° by x_1—condition for no change in band length—in the expression for the mixed state which under condition given in equation (7) gives:

Component 2:

$$\Delta S_2^\circ = -L(1-x_1)\left[\frac{x_2}{1-x_1}\ln\frac{x_2}{1-x_1} + \left(1-\frac{x_2}{1-x_1}\right)\ln\left(1-\frac{x_2}{1-x_1}\right)\right]$$

Component 1:

$$\Delta S_1^\circ = -L\left[\frac{1}{R_1}x_1 \ln x_1 + (1-x_1)\ln(1-x_1)\right]$$

Hence it may be shown that

$$\Delta S_1^\circ + \Delta S_2^\circ = \Delta S^\circ - L\left[\frac{1}{R_1}x_1 \ln x_1 + (1-x_1)\ln(1-x_1) + x_2 \ln x_2 - (1-x_1)\ln(1-x_1) + (1-x_1-x_2)\ln(1-x_1-x_2)\right]$$

or simply,

$$\Delta S^\circ = -L\left[\frac{1}{R_1}x_1 \ln x_1 + x_2 \ln x_2 + (1-x_1-x_2)\ln(1-x_1-x_2)\right] \quad (8)$$

Comparing equation (6) and (8) we find for the simple binary system under consideration that entropy of unseparated system is exactly equal to the entropy of the separated system, thereby showing that the chromatographic process is an isentropic process which takes place in a reversible manner.

References

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