

## Short Communication

# Golay's paradox: linear *versus* non-linear chromatography

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### ABSTRACT

**Golay** in 1964 posed the paradox that it should theoretically be possible to conduct an operation of single-component chromatography with linear isotherm and high column loading in such a way that the entropy of the system is decreased. The paradox is resolved by showing that the concentration dependence of the flow-rate, invoked by **Golay**, renders the system non-linear despite the linear isotherm. The result of the non-linearity is that one of the concentration variations spreads, instead of remaining sharp as it would in linear chromatography and as was assumed by **Golay**. This spreading negates the entropy decrease.

**Golay** [1] in 1964 posed a paradox, showing that gas chromatography under idealized conditions can defy thermodynamics by decreasing the entropy of a closed system. It puzzled all those attending the *Gas Chromatography* conference at which it was presented, and its resolution [2] still seems not to be generally known [3]. In abbreviated form and in our current language of wave theory (see, e.g., ref. 4) the paradox can be formulated as follows:

A gas chromatographic column is loaded initially with two successive flat-top bands of the same solute; the bands are adjacent, and the solute concentration is higher in that on the upstream side (see Fig. 1). The concentrations are high enough for the volumetric flow-rate to be axially non-uniform. Specifically, the flow-rate is higher at higher solute concentrations [5]. This effect, sometimes called "sorption effect", arises because any solute present must be transported through the column cross-section in addition to the carrier gas, so that a higher molar and

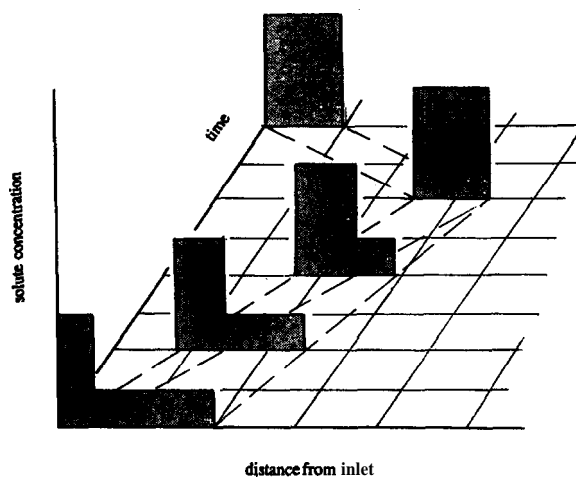


Fig. 1. Initial, intermediate, and final concentration profiles as postulated by **Golay**, shown in distance-time field; return of concentrated band to starting position upon flow reversal is included; thin dashed lines are wave trajectories in distance-time plane (schematic).

thus, in gases, volumetric flow-rate is required where the solute concentration is higher. The effect becomes significant at moderate to high mole fractions of solute. The isotherm is assumed to be linear. Since non-idealities—specifically: finite mass-transfer rates, non-plug flow, and axial **diffusion**—cause waves in linear chromatography to spread in proportion to the **square root** of traveled distance (see, e.g., ref. 6), the column and the bands need only be made sufficiently long for such spreading to remain an insignificant fraction of the band lengths upon passage through the column. Accordingly, for the purpose at hand, bands can be assumed to move like “box cars” between waves that remain practically sharp. Granted this point, the band of higher concentration, traveling faster because of the sorption effect, will “swallow up” that of lower concentration on its downstream side, so that eventually all of the solute will be in a single band at the higher concentration (see Fig. 1). The initially more dilute band has in effect been concentrated, and that amounts to a decrease in entropy! In **Golay’s** imaginary world of “frictionless chromatography”, this is achieved at no expenditure in energy or free energy. **Golay** does not say so but, granted his assumptions, flow could be reversed to move the single, high-concentration band back box-car style to where the two bands started, making it even more apparent that enrichment has been achieved at no cost (see Fig. 1).

The resolution of this paradox is simple and requires neither mathematics nor thermodynamics [2]. **Golay** makes mutually exclusive assumptions when he postulates that (1) waves spread in proportion to the square-root of traveled distance, and (2) the flow-rate is higher at higher concentrations. If condition 2 is met, the rear of the concentrated band cannot remain sharp: it contains high concentrations ahead of low ones, that is, faster concentrations ahead of slower ones, and therefore it spreads **in proportion to traveled distance** (see Fig. 2). This proportional spreading is in addition to the supposedly negligible square-root spreading caused by any non-idealities, and is an effect that **cannot** be suppressed by a scale-up to greater lengths of column and bands. As seen in Fig. 2, the real

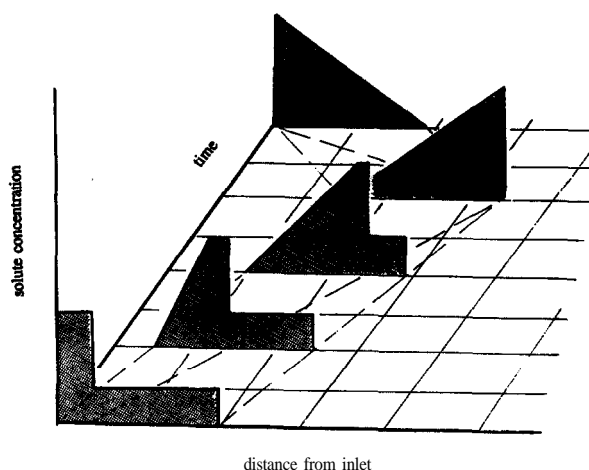


Fig. 2. Actual initial, intermediate, and **final** concentration profiles as resulting from sharpening and spreading behavior of non-linear waves; return of solute to starting position upon flow reversal is included (schematic; the slanting profiles are not necessarily linear; the high-concentration plateau may disappear earlier, or a portion of it may survive).

result of the operation is an asymmetrical peak or band with sharp front and diffuse rear, rather than **Golay’s** “box car” band of uniform high concentration. By a reversal of the flow direction, the peak or band could be moved back to where the two bands had started. The diffuse flank would then regain its sharpness because, in it, the faster, higher concentrations are now upstream of the slower, lower ones. However, in the other, still sharp flank the situations is the reverse, and this flank would now spread (see Fig. 2). Thus, the whole operation achieves no more than trading the initial step profile for a continuously slanting one, with no decrease in entropy.

It is true that condition 1 **can** be met, for instance, at concentrations low enough to make the sorption effect negligible. However, this would invalidate assumption 2, and the bands would move side by side without change in shape, that is, **Golay’s** effect would not materialize.

The spreading rear flank of the concentrated band is what is commonly called a **nonsharpening** wave (or rarefaction wave in gas dynamics). In ideal non-linear chromatography in the absence of the sorption effect, nonsharpening

waves are well known to arise as a result of an isotherm curvature that causes leading concentrations in the wave to move faster than trailing ones [4,7,8]. For instance, a solute band has a nonsharpening rear if the isotherm is of Type I (*i.e.*, with negative curvature), and a nonsharpening front if the isotherm is of Type II (with positive curvature). In **Golay's** case, the isotherm is assumed to be linear. However, *any* effect that makes leading concentrations in a wave travel faster than trailing ones (granted non-idealities are negligible) obviously produces proportional spreading. It is immaterial whether the cause is an isotherm curvature or the sorption effect. If the sorption effect is significant, it could be compensated by a slight Type II curvature of the isotherm [9] so as to meet **Golay's** postulate 1. Then, however, the result is the same as with a linear isotherm and negligible sorption effect: The bands move side by side without change in shape.

**Golay** admits the existence of non-idealities, being content with rendering their effect negligible by scale-up to very large column and band lengths. However, one could argue that, in a mathematical world of strictly ideal chromatography, the intermediate concentrations of the nonsharpening wave at the rear of the concentrated band (*i.e.*, those that form the spreading wave in Fig. 2) never come into existence, so that their velocities remain immaterial. The wave could then keep moving as a discontinuity, and the paradox would remain. Indeed, such behavior is described by a mathematically correct "weak solution" [10,11] to the differential mass balance and overall conservation of matter, analogous to the weak solutions that describe the shocks (*i.e.*, traveling concentration discontinuities) at the front of the low-concentration band and between the two bands. That the weak solution for the nonsharpening wave can have no physical reality can be shown by a rather involved argument that proves it would violate the second law of thermodynamics [12,13]. An alternative and much more simple argument is that mathematics of ideal chromatography is of practical interest only insofar as it provides a reasonable approximation to real behavior. This it does if it constitutes an asymptotic solution to

real chromatography with non-idealities made infinitesimally small. The weak solution for the nonsharpening wave does not meet that criterion because any **non-ideality**, even if only infinitesimal, lets the intermediate concentrations become physically realized and so causes the wave to spread in a proportional pattern rather than remaining ideally sharp [4].

**Golay** himself was on the right track when seeking an analogy with shocks in gas dynamics. He concluded correctly that the wave between the high- and low-concentration bands would have to be a shock -that is, a wave which sharpens or remains sharp despite the spreading effect of non-idealities- and so should produce entropy in the same way as shocks in compressible fluids are known to do. However, he was unable to resolve his paradox because he missed the key piece of the puzzle by not recognizing the rear of the high-concentration band as a nonsharpening wave (rarefaction wave in gas dynamics). Thus it can be said that, ultimately, the paradox arises from a failure to realize that, despite a linear isotherm, the sorption effect makes the system non-linear and thereby invalidates the familiar tenet of linear chromatography that all waves spread in proportion to the square root of traveled distance.

Much has been written about the complex thermodynamics of entropy production by traveling waves [12-14]. The only aspect of interest in the present context is the following. In **Golay's** "frictionless" world and granted the assumptions of ideal chromatography, the travel of a nonsharpening wave is entirely reversible and so produces no entropy; this is because a reversal of the direction of flow would make the wave self-sharpening and so let it regain its original sharpness while returning to its starting point. Likewise, the travel of an initially diffuse but self-sharpening wave remains reversible because flow reversal would cause the wave to spread to its original diffuseness. However, this is true only *as long as the wave has not yet sharpened into a shock* (*i.e.*, become a discontinuity). The travel of a shock is irreversible and so produces entropy even in the ideal world because a reversal of the flow direction would make the wave nonsharpening and cause it to spread. Entropy

production or the lack of it can also be linked to information theory, as **Golay** attempted but did not fully succeed: in the ideal world, any wave that is not a shock carries with itself complete information about its degree of sharpness at any previous point or time; in contrast, the shock "forgets" much of its history, not remembering for how long it has traveled as a shock. The longer it may have done so, the greater is the uncertainty about its original degree of sharpness.

It may seem paradoxical that a spreading (nonsharpening) wave does not produce entropy whereas a traveling shock, remaining sharp, does. As to the nonsharpening wave, we cannot equate spreading with mixing or diffusion effects. Any spreading caused by non-idealities *is* a dispersion in the usual sense, and so is irreversible and produces entropy. However, the spreading caused by the isotherm curvature is of a quite different nature: Being reversible, it does not increase the disorder of the system; we might say the system has "stored" the free energy needed to make the wave sharp again. As to the shock, it travels without change of its profile, not creating any apparent disorder, so how come it produces entropy? The answer is that the shock must not be viewed all by itself: It leaves the system in a different state from which no return

to the original state is possible without expenditure of free energy. For instance, if the shock has saturated a sorbent (e.g., acted as the front of a peak), stripping (at the rear of the peak) would entail a nonsharpening wave, for a net result of solute dispersion, for which the shock is ultimately responsible.

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