One of the most important occurrences in chromatographic systems is the broadening of peaks as compounds move through the chromatographic column. For example, if we examine Figure 18 in which both sets of peaks have the same retention times but different extents of broadening, we see that the set of conditions that produce the narrower set of peaks (Figure 18b) resulted in “better” or more efficient chromatography. What we observe in the chromatogram with less peak broadening is that the peaks are fully resolved and that we could fit more peaks into a similar window of time in the chromatogram. An ideal chromatographic system would therefore produce peaks that were straight line spikes in which no broadening occurred (Figure 18a).

There are specific processes that occur in chromatographic systems that cause peaks to broaden. It also turns out that these processes are often influenced by experimental variables that we may have some control over. Contributions to broadening in chromatographic systems can be divided into two broad areas of concern. One is the contribution from what is known as **dead volume**. Dead volume refers to all the volume in a chromatographic system from the injector to the detector other than the column. Remember, the separation only occurs in the column. All other volumes (tubing used to connect components, volume within the detector cell, etc.) have the ability to contribute to peak broadening but not to the separation. One general goal then is to try to reduce the total dead volume to as small a quantity as possible. In liquid chromatography this involves using very narrow internal diameter tubing and short lengths of tubing to connect the components, using small-volume detector cells, etc. The fittings that are used to connect pieces of tubing together or components to each other have been designed specifically to reduce the dead volume to minimal levels and in ways that do not promote mixing and broadening.

The other source of broadening is within the column. If you were to examine state-of-the-art columns that are used today in gas and liquid chromatography, it turns out that there are several features of their design that lead to significant reductions in peak broadening. In other words, these columns represent the best we can do today to reduce the broadening of peaks, and therefore represent the most efficient column technology. It is worth taking the time to understand the various contributions to peak broadening that occur within the chromatographic column and to examine the ways in which current gas and liquid chromatographic columns have been designed to minimize these effects.

There are four general contributions to broadening within chromatographic columns. These are known as:

- longitudinal diffusion
• eddy diffusion
• mass transport broadening in the stationary phase
• mass transport broadening in the mobile phase

Before moving on, it is worth remembering back to two fundamental criteria we talked about with regards to chromatographic columns, the number of theoretical plates (N) and the reduced plate height (h). Remember that a column with more plates, or better yet a column with a small reduced plate height, was more efficient and provided better separations. We can therefore use the reduced plate height as a determining measure of the efficiency of a chromatographic column. **The smaller the value of h, the more efficient the column.** What we will develop as we analyze the four contributions to broadening above is an equation, which was first known as the van Deemter equation (J. J. van Deemter described the first treatment of this for chromatographic systems in 1956), that relates these four terms to the reduced plate height.