The van Deemter Equation:

A Three Act Play

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Playbill

All too rarely does science meet with society in any kind of theatrical forum. To be able to convey difficult scientific facts and principles in an engaging and entertaining fashion while still preserving the truth of the science is no small feat. Some recent examples of resounding successes in this arena include the play *Oxygen*, written by chemists Carl Djerassi and Roald Hoffman, and *Copenhagen*, the 2000 Tony Award winning play by Michael Frayn. The first of these plays struggles to uncover the discoverer of oxygen: Joseph Priestly, Antoine Lavoisier, or Carl Wilhelm Scheele, so that the first-ever retro-Nobel prize can be appropriately awarded, while the second speculates on the events that transpired during a hypothetical meeting in 1941 between the two long-time friends and brilliant physicists, Niels Bohr and Werner Heisenberg, who suddenly found themselves on opposite sides of WW II.

Your job is to mount the first-ever North American stage production of the important and yet often times under appreciated van Deemter equation, which plays a pivotal role in understanding chromatographic separations in chemistry. This is a daunting task, especially given the rave reviews to which a similar performance played recently in Europe:

> *Brilliant. Stunning choreography and synchronization. Never before have there been more challenging roles for solute and solvent molecules.A feel-good performance of a vital piece of chemistry.*

> *Crystal clear depiction of three major contributions to band broadening in chromatography. van Deemter would be proud.*

The van Deemter Equation

Act I: Eddy Diffusion

Setting the Scene: Eddy diffusion leads to peak broadening in chromatography due to the different lengths of time it takes solute molecules (of the same type) to travel through the column by way of different paths.

Casting: A minimum of about 20 and a maximum of about 35 cast members are required for this scene. Six will be selected as solute molecules and the remainder will be stationary phase particles.

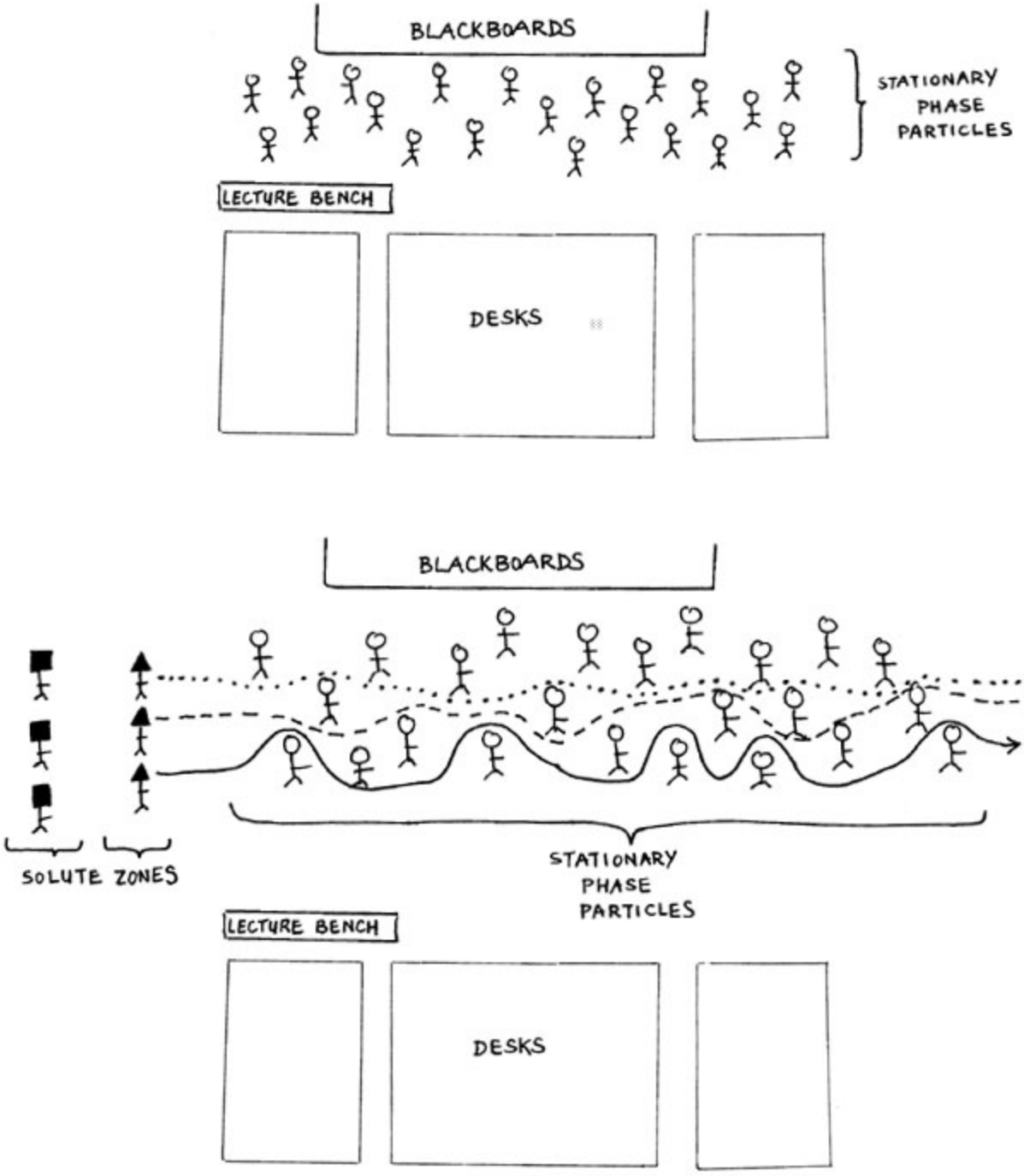
Action: **Stationary phase particles** must appropriately arrange themselves across the front of the classroom so as to form a chromatographic column. **Solute molecules** will form two "zones" or "bands" of three members each (with each zone or band representing a different kind of solute or a different sample component). It must be clear that the three members of each zone are identical molecules. Although the three molecules in one solute zone will begin to "elute" or travel through the chromatographic column together, they will arrive at the other end at different times due to their different paths traveled through the stationary phase particles. Each zone of solute molecules will contain one molecule that travels through the chromatographic column as directly as possible, one molecule that travels through the chromatographic column with some detours, and one molecule that travels with many detours. After one zone of solute molecules has completely eluted, the other zone will similarly travel through the column, thus re-enacting travels similar to those of the first zone.

Questions to consider before the scene (Act I):

1. Why is it important for the three solute molecules in each zone to be identical (even though the solute molecules between zones may differ)?

2. What physical aspect of a chromatographic column can lead to the existence of different routes or paths through that column?

Act I


BLACKBOARDS
STATIONARY PHASE PARTICLES
LECTURE BENCH
DESKS
BLACKBOARDS
SOLUTE ZONES
STATIONARY PHASE PARTICLES
LECTURE BENCH
DESKS

The van Deemter Equation

Act II: Longitudinal Diffusion

Setting the Scene: Diffusion along the length of the chromatographic column leads to peak broadening due to the "spreading out" of the solute zone. Molecules naturally diffuse from regions of high concentration (near the center of a solute zone) to regions of low concentration (expanding the edges of the zone further and further out). The longer the solute zone is in the column the more time there will be for longitudinal diffusion to occur, and hence, the greater the extent of zone broadening.

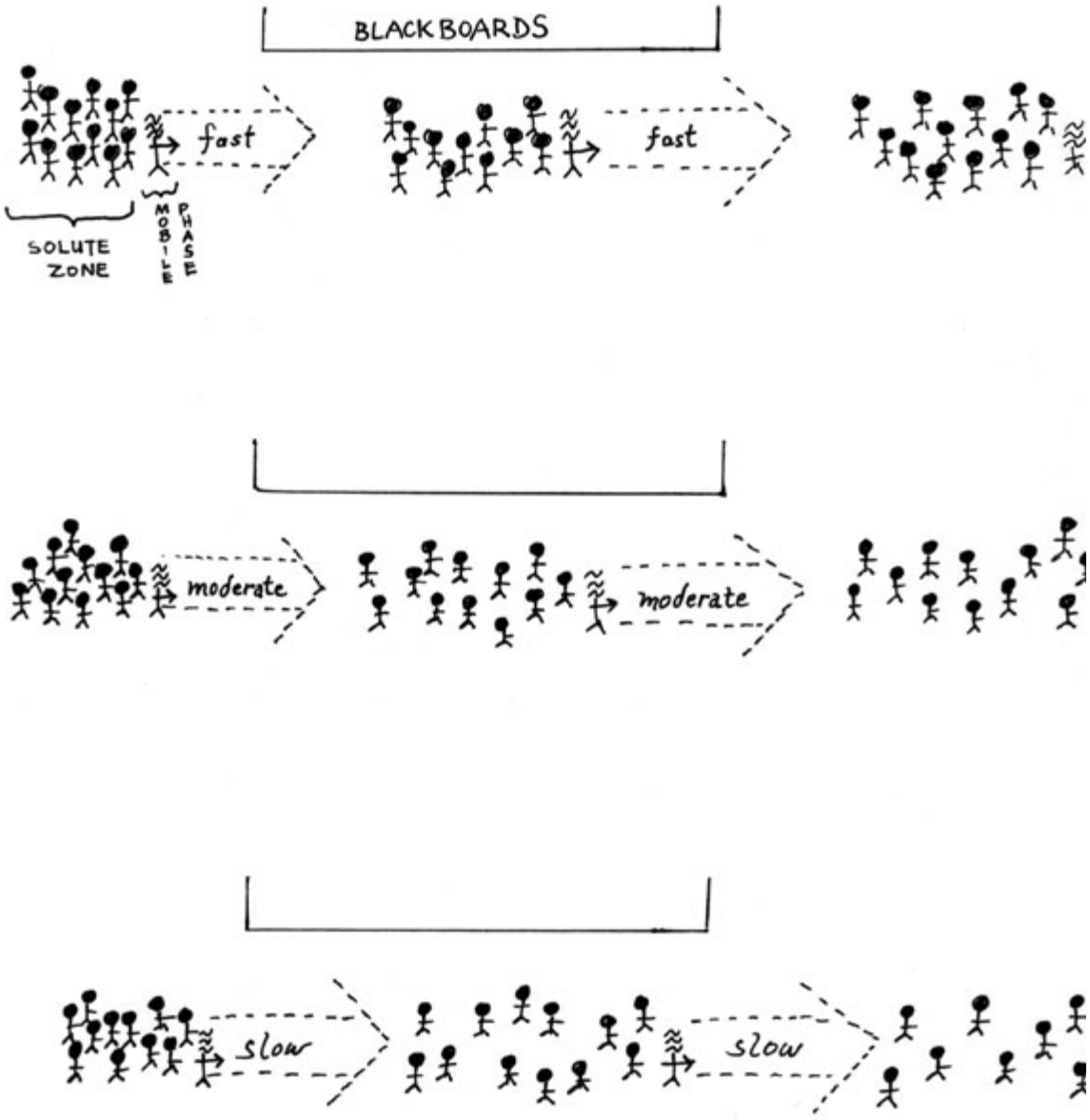
Casting: A minimum of about 20 and a maximum of about 40 cast members are required for this scene. Cast members should be divided into three equal subgroups, each of which is composed entirely of identical solute molecules with the exception of one member of each subgroup who will represent the mobile phase.

Action: **Solute molecules** within each subgroup will assemble in a tightly packed (highly concentrated) arrangement, with little space between group members. Action will begin with the *first subgroup* of solute molecules collectively moving *quite rapidly* across the front of the room, representing elution of the solute zone through the column. The **mobile phase** representative will "usher" the subgroup (or zone) of solute molecules along, setting a constant fast pace for elution. As the group travels across the room, they will begin to spread apart from one another. This spreading should be only very slight for the first group, so that by the time they reach the far side of the room they will still be in a fairly tightly packed arrangement.After the first subgroup has "eluted", the second subgroup will likewise begin to travel across the room, beginning in their tightly packed arrangement. However, the collective travel of the second subgroup will be *slower* than the first subgroup, as established by the slower pace kept by the accompanying mobile phase representative. This slower pace will allow more time for the solute molecules to spread apart from one another, and so by the time they reach the far side of the room, their spreading will be more extensive than that of the first subgroup.Finally, the third subgroup will begin to collectively travel across the room, keeping pace with the *slowest moving* mobile phase representative yet. Consequently, by the time the third solute zone reaches the far side of the room, they will be more spread out than either of the first two "zones."

Question to consider before the scene (Act II):

1. Why is it important for the three subgroups to contain the same number of solute molecules (and for the three subgroups to represent the same type of solute) before beginning their travels through the chromatographic column?

Act II


BLACKBOARDS
fast
fast
SOLUTE ZONE
MOBILE PHASE
moderate
moderate
slow
slow

The van Deemter Equation

Act III: Rate of Mass Transfer

Setting the Scene: Partitioning of the solute between the mobile and stationary phases may require more or less time (the equilibration time) depending upon the nature of the stationary phase, the partition coefficient, the diffusion coefficient of the solute in the stationary phase, and other factors. From a practical point of view, this means that resistance to mass transfer may differ at various sites in the stationary phase, thus leading to peak broadening.

Casting: A minimum of about 20 and a maximum of about 40 cast members are required for this scene. Six cast members will be **solute molecules**, and the remaining cast members will be split equally amongst **stationary phase particles** and **mobile phase molecules**.

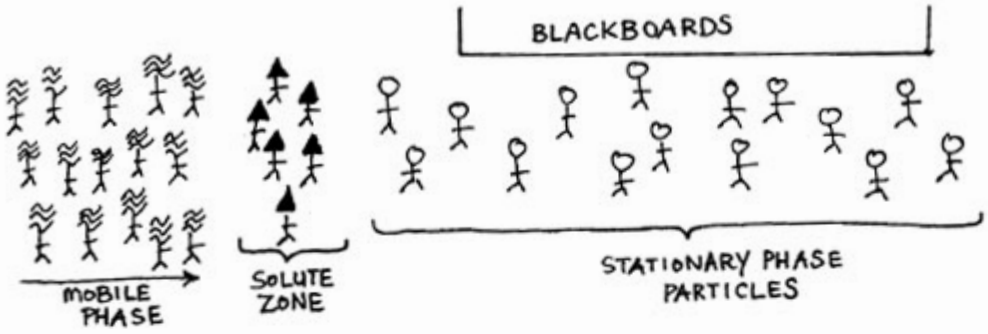
Action: **Stationary phase particles** must appropriately arrange themselves across the front of the classroom so as to form a chromatographic column. They will (as their name implies!) remain stationary throughout the act, but will periodically interact with solute molecules (by grasping arms or hands), as appropriate. **Mobile phase molecules** will steadily depart from their group, a few at a time, to travel through the "chromatographic column" of stationary phase particles, thereby achieving a constant "flow" through the column. If a mobile phase molecule happens to encounter a solute molecule on its travels, it may "carry" that solute molecule through the column with it (appropriately shown by linking arms or holding hands rather than physically carrying!) for some distance, until such time as the solute molecule "chooses" to interact again with a stationary phase particle. At this point, the mobile phase molecule will continue to pass through the column, alone now, until it may or may not encounter another solute molecule with which it may or may not interact. **Solute molecules** will begin as a cohesive group of identical molecules at the head or front of the chromatographic column formed by the stationary phase particles. Each solute molecule will be carried onto the column by "linking up" with a mobile phase molecule. After a short distance, the solute molecule will preferentially interact with a stationary phase particle for some short time before linking up again with another mobile phase molecule. This "partitioning" between mobile and stationary phases will continue until the solute molecules have made their way through the column. In this example, the time spent with any given stationary phase particle may differ from the time spent with any other, and likewise, the time spent with any given mobile phase molecule may differ from that spent with any other. Despite these critical variations, each solute molecule should be mindful of the progress of other solute molecules through the column, and should pace their travel accordingly.

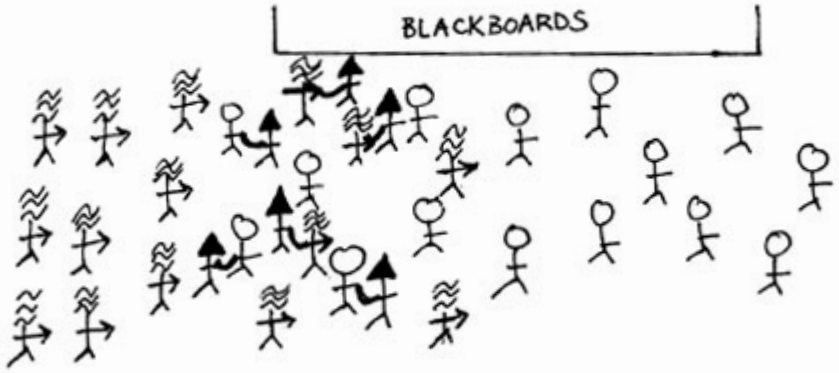
Questions to consider before the scene (Act II):

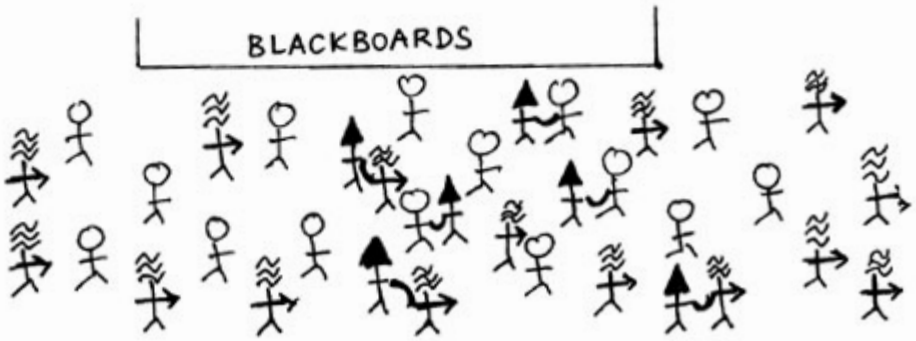
1. Why is it important for the solute molecules to be identical (i.e., how would the "separation" be affected if they were different)?

2. What determines the nature of interaction between a solute molecule and a stationary phase particle, or between a solute molecule and the mobile phase?

Act III


BLACKBOARDS
MOBILE PHASE
SOLUTE ZONE
STATIONARY PHASE PARTICLES


BLACKBOARDS


BLACKBOARDS

After the Scene:

Some Questions to Consider

Act I

1. *In Act I: Eddy Diffusion, why did the three molecules in each "zone" or solute group travel at slightly different rates through the column, even though the molecules themselves were identical? How could this effect be minimized or eliminated?*
2. *Would the phenomenon that you described in answer to #1 be affected by the velocity of the mobile phase, and if so, how?*

Act II

3. *In Act II: Longitudinal Diffusion, each group or zone consisted of the same number of identical solute molecules (representing the same initial concentration). What aspect of their travel through the column resulted in different extents of spreading (or longitudinal diffusion) for each of the three solute zones? Consequently, how does the velocity of the mobile phase affect the zone broadening in this case? How could broadening be minimized in this case?*

Act III

4. *Even with mobile phase molecules traveling at a constant speed via regular paths through the chromatographic column in Act III: Resistance to Mass Transfer, did the six identical solute molecules arrive at the far end of the column at the same time? If not, why not?*
5. *Would the velocity of the mobile phase have any impact on the phenomenon that you described in answer to #4? If so, what would that effect be?*