Arrows and the New York City Subway: Using Analogies to Explain Entropy and Activity

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INTRODUCTION

Possibly one of the most difficult courses to teach in the pharmacy curriculum is physical pharmacy. Within the course, the most difficult topic is thermodynamics and, within that, the subject of entropy. There are many reasons for this. Physical pharmacy is usually taught in the first professional year (at least this is the case in our program). Students in this year are more difficult to teach than those in any other year. Having just completed the preprofessional years, where the focus of teaching is more general, they enter the professional phase of their course work not quite accustomed to the notion that pharmacy is like nothing else they have ever studied. In a very real sense, it is as if they are beginning college all over again.

While there are several tough courses facing the first-year students, the one that makes the least sense to them from the point of view of applicability to the pharmacy program is physical pharmacy. The other courses – biochemistry, physiology, microbiology, pharmaceutical calculations – are more clearly precursors for material yet to come. But the principles taught in physical pharmacy have, at least in the mind of today's student, little relevance to the practice.

Among the topics taught in the course, there are some deemed

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more relevant than others, and these are, therefore, easier to teach. Kinetics, of course, is seen as basic to the understanding of pharmacokinetics, which is to come later. Although the concepts of rate, order, and half-life are a little difficult, it requires little effort to clarify them for the students. This is true of the principles of rheology. Every student can be made to realize that the knowledge of the processes of flow and the basics of viscosity are important to the understanding of the manufacture of semisolid and heterogenous liquid dosage forms. The topic of dissolution and properties of solutions can be shown to have a good deal of relevancy with respect to dosage form design and biopharmaceutics. But thermodynamics is quite different. The concepts involved are sometimes too abstract even for chemistry majors, let alone pharmacy students who are hard put to place enthalpy, entropy, and free energy into the great scheme they perceive will lead to licensure and the dispensing of pharmaceuticals. Of the myriad topics in thermodynamics, the two most challenging to teach are entropy and the concept of activity. As a physical chemist who has somehow found a two-decade career in pharmacy, I discover myself at once eagerly awaiting the challenge and dreading the appearance of the topics in the lecture schedule.

Entropy

The concept of entropy or disorderly conduct is best approached, at least under our particular circumstances, from a nonmathematical view. I usually address the subject from the point of view of total energy in a system and that portion of the energy that is available to drive the system. I attempt to relate this to the stability of suspensions and emulsions, diffusion, solution characteristics, and certain electrochemical and complexation phenomena that are related to the design and analysis of dosage forms.

I then pose the question as to why any of the energy should be *unavailable*. I explain that if a system is to do useful work, the various parts of the system must be working in concert (i.e., in the same direction), especially if they are working against a contrary force. One can, of course, refer to the parts more specifically as molecules, atoms, etc.

Clearly, all the parts of the system will not be facing in the same direction at any given time. There is, in fact, a randomness in the direction and motion of the various parts. This randomness is more prevalent in a gas than in a liquid and more so in a liquid than in a solid. (It is useful to have reviewed states of matter before attempting to teach thermodynamics.) The greater the randomness, the more energy is wasted or unavailable for useful work, and entropy is a measure of, and is proportional to, the amount of randomness or disorder in the system.

At the same time, increased temperature increases molecular motion (or the motion of the parts of the system) and therefore makes it more difficult to order the system. Hence, the unavailable work is a function of both temperature and entropy and when subtracted from the total energy, yields the available, useful, or free energy of the system:

$$G = H - TS$$

Where, in the usual symbols, G is the Gibbs free energy, H is the enthalpy or total energy, T is absolute temperature, and S is the entropy.

Finally, entropy is related to probability. (It is usually useful to have reviewed some basic statistics by this point also.) I use an example of arrows being tossed in the air (although any pointed object will do) and coming down randomly with their points scattered in every direction—the greatest probability, the greatest disorder, the greatest entropy. Since most arrows in this world behave the same way, it is an easy step to convey Clausius' thoughts (without mentioning him) that the entropy of the world tends toward a maximum (1).

Activity

For those students who have survived the laws of thermodynamics, the other conceptual hurdle is the notion of activity. Again, the concept is foreign to the typical student's experience, and its relevance is called into question. The latter can be related to the principles of diffusion and equilibrium, which in turn, can be related to the design and stability of dosage forms, as well as the processes of biopharmaceutics.

In terms of experience, I like to equate activity to effective concentration and express it in terms of an analogy that I find useful in clarifying the idea (2). As the reader will see, this scenario works better in our college, which is located in New York City, than it might in a school located in a more rural area. I ask the students to imagine a subway car in which there is only a handful of passengers. When the train stops, each passenger can easily exit the car unimpeded; thus, each has an equal impact on the environment; i.e., the area outside the car. Then I ask them to imagine a typical rush-hour situation (which, of course, New York residents have little difficulty in doing). Now when the train stops, those passengers nearer the doors have little difficulty in exiting (in fact they sometimes have no choice). Their activity or escaping tendency (the thermodynamic term) is much greater than the escaping tendency of those in the middle of the car, and their impact on the environment will be much greater than the impact of those in the middle. Thus, in the first situation, the activity of all the passengers (molecules, atoms, etc.) is essentially identical and equal to the concentration of passengers in the car. This is analogous to the infinitely dilute solution, where the activity coefficient is unity. In the rush-hour case, the activity or escaping tendency of the various passengers (components) is quite disparate, with an activity coefficient not equal to one.

While, admittedly, both lessons involve some simplistic analogies, it is my view that the understanding of a principle is the major goal of teaching and that the method used in achieving that understanding is essentially irrelevant. Further, I do not believe that this view is unique. The use of analogies has been a useful pedagogical tool from the days of Aesop for teaching everything from philosophy to physics to pharmacy.

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