Equilibrium partitioning of organic compounds

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Mine sweeper for environmental chemists - not a game!

Question: Does it make a difference whether dogs are trained on a small or a large quantity of explosives?

Answer: Does half a cup of coffee smell differently than a full cup of coffee? The equilibrium gas phase concentration of explosives above a few crystals of TNT is the same as it is above a large amount of TNT. This is consistent with what we learned about equilibrium partitioning: only the mass of the solid phase changes during evaporation while the concentration in the solid phase stays constant. Hence the equilibrium concentration in the adjacent gas phase will also remain constant. Therefore, thermodynamically speaking, the answer should be **NO**.

However, there is a kinetic effect as well. As the amount of the explosive chemical increases, so does the total surface area of the chemical (i.e., the interface between the pure crystalline chemical (phase 1) and air (phase 2)). The time required to reach equilibrium concentrations in the air decreases with increasing surface area. In other words, the larger the amount (and thus the interfacial area) of the explosives, the faster is the partition equilibrium attained.

In the training situation one needs to work with TNT samples in open containers. Close to the sample one may still find the equilibrium concentration of the explosives in air even if there is only a small piece of explosive. However, farther away from the sample, the explosive vapors quickly become diluted by turbulent air. In this case, the actual air concentration very much depends on the kinetics with which the explosive molecules are transferred into the air. These kinetics increase with the interfacial area of the explosive sample. In order to train animals under standardized and reproducible conditions it would be good to minimize the effect of dilution by turbulences. To this end, it is advisable to either bring the noses of the dogs in very close contact to open samples or to present the samples in containers that have a small opening at which the dogs smell.

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