# Axel's dilemma

## Answer:

**Background:** Volatilization of a chemical from its own pure liquid to the gas phase is an ordinary partition process. The only thing that is special is, that the concentration of the chemicals in its own pure phase is always constant. That means that the mass and volume of the pure phase becomes larger or smaller by condensation or volatilization, respectively, but the concentration in the pure phase always stays constant. Thus there is only one equilibrium gas phase concentration of each chemical above its pure phase at a given temperature. The equilibrium between the pure phase and its gas phase is hence fully characterized by just reporting the gas phase concentration. If this equilibrium gas phase concentration is expressed as a partial pressure (see ideal gas law) then we call this the saturation vapour pressure of the respective compound.

**For the answer of the above question it is helpful to distinguish two extreme situations:** a) Liquids (i.e., pure condensed phases) that have only a very small tendency to partition into each other because they gain much more energy out of interacting with molecules of their own kind and b) liquids that mix completely because they gain similar interaction energies with other molecules as they do with molecules of their own kind.

**In case a)** molecules from each liquid would indeed partition into the gas phase as if they were alone in the system. Assuming ideal gas, the resulting total pressure in the gas phase would then indeed equal the sum of all individual saturation vapour pressures. This would be true no matter whether the liquids were present in 10 different flasks or whether they were all put into one flask where they would then still form 10 separate pure phases. However, if each of the 10 liquids has a vapour pressure of 50 000 Pa, then the gas phase would become so dense that there were no longer ideal gas phase conditions. Consequently, the real total pressure would be somewhat smaller than the sum of the individual partial pressures due to attractive interactions between the gas phase molecules. This case a) remains purely hypothetical though: there are no ten (organic) liquids with negligible tendencies to partition into each other.

**In case b)** the chemicals will not only partition out of their own pure phase into the gas phase but from there they will partition into all the other liquids. At equilibrium, all ten flasks would contain molecules from all 10 liquids in the same concentration ratio. So the resulting liquid would be the same as if we had mixed all liquids together in one flask right at the beginning. What is the consequence now for the equilibrium vapour pressure? The tendency for any single molecule to escape out of these liquid mixture(s) into the gas phase

must be the same as compared to their tendency to escape out of their own pure liquids (because we have assumed for case b) that the strength of intermolecular interactions in all phases to be the same). But the concentration of each chemical in the liquid mixtures is only 10% of what it was in their pure phases. Hence, their individual equilibrium vapour pressures can also only be 10% of the vapour pressures above the pure phase. Consequently the total vapour pressure of all 10 chemicals is identical to that of each individual pure chemical, i.e. 50 000 Pa.

Reality will typically lie somewhere between these two extremes a) and b) depending on which chemicals are chosen. In fact, the total vapour pressure could even be somewhat smaller than the individual vapour pressures in case that the chemicals prefer each other over their own pure liquid phase.

**See Chapter 4 for more information about which chemicals like each other and which do not.**