Equilibrium partitioning of organic compounds

Some fundamentals ..

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2 Phase system: condensed phase and gas phase

In a closed bottle that contains water and air, some water always resides in the gas phase. The exact number of water molecules in the gas phase strongly depends on the temperature of the system. We can say that the gas phase is saturated with water or: the gas phase is in equilibrium with the aqueous phase with respect to the partitioning of water molecules. The same would be true if the bottle contained oil and air. In this case, the saturation concentration of oil molecules in the gas phase would differ from that of water molecules.

Both, the water and the oil molecules gain energy from the mutual interactions with their neighboring molecules in their condensed phases. In the gas phase, molecules do hardly gain any energy from interactions with neighboring molecules because the molecules are - averaged over time - too far apart from each other. But then why do some water or oil molecules in equilibrium still reside in the gas phase? The reason for that is the thermal movement of the molecules. Temperature causes molecules to move: this includes various rotations and vibrations within the molecule but also a movement of the entire molecule within space. The higher the absolute temperature, the faster the movement of the molecules. In a phase in which the molecules are not subject to any kind of interactions with one another, i.e. an ideal gas phase, the thermal energy causes all molecules to evenly spread and fill the available space. This is illustrated in the following animation: Also, notice that thermal energy causes molecules to spread evenly independent of the nature of the molecules and no matter whether one looks at a single type of molecules or a mixture:

http://www.chemit.co.uk/uploads/java/rsc_diffusion/applet.htm

Condensed phases can only exist if the interaction energy between the molecules of the condensed phase is higher than their kinetic energy. But then why do some water molecules still reside in the gas phase if a condensed water phase is present? At a given temperature water molecules (and all other molecules as well) do not all attain the same kinetic energy but there is a distribution of energies. Some molecules are faster and some are slower. Check out the animation below. It demonstrates the kinetic theory of gases. The color of each molecule indicates the amount of kinetic energy it has. You choose different examples from the setup menu.

Equilibrium_04

http://www.falstad.com/gas/

If a molecule in phase I hits the interface to another phase II then those molecules whose kinetic energy is high enough to overcome the attractive interaction within phase I will enter the adjacent phase II even if there are no attractive interactions in the other phase II (as in the gas phase). This explains why some molecules always reside in phases in which they gain less interaction energy than in other available, adjacent phases.

Increasing the temperature hence has two concurrent effects: it lowers the intermolecular interactions (i.e., the interactions BETWEEN molecules) and it increases the thermal energy and hence the movement of molecules. As a result, the molecules have a higher tendency to equally spread in the complete system. Therefore, an increase in temperature favors an equal distribution of all molecules between all phases.

In general, any partition equilibrium is the result of two counteracting factors: attractive interactions between molecules that hold them together and the kinetic energy that makes them move apart.

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