Evaporation is the process in which a liquid slowly transfers from the condensed (liquid) phase to the gas phase—like the peaceful scene pictured above.

If temperature is increased, heat transfers more energy to the liquid—giving molecules the power to escape from the liquid’s surface. This rise in temperature therefore increases the transfer from liquid into the vapor phase.

The transfer from the condensed to vapor phase (and vice versa) are at an equilibrium based upon temperature. This also means that if the temperature is lowered, the more the compound will condense into the liquid phase—like a cold beverage on a warm day.

The boiling point is the temperature where liquid has enough energy that molecules transferring into the vapor phase exert a pressure that is equal to the outside pressure. This allows molecules anywhere—not just the surface—to transfer to the gas phase.

This equilibrium has a direct impact on temperatures in gas chromatography. If the oven temperature is too cool, a compound will spend most of its time condensed in the stationary phase. Only a very small amount that can evaporate will transfer down the column.

Conversely, if the temperature is very high then the equilibrium will shift in the opposite direction. The compound will spend all of its time in the vapor phase and not condense into the stationary phase.

Gas chromatography works when a compound can transition freely both into and out of the stationary (condensed) phase. Only when the compound is condensed can it interact with the stationary phase. Only when the compound is in the vapor phase can the mobile phase
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push the compound along the column to the detector.

Very volatile compounds will not interact with the column phase if the temperature is too high above the boiling point. Therefore, the temperature needs to be lowered to get favorable interactions with the phase. Obviously, too low a temperature will cause the entire amount of compound to be condensed. That doesn’t work well because it is the transition from the liquid phase to the gas phase and back which is responsible for the separation.

In fact, that is the idea for the theoretical plate. Each transfer (in–out–and back in) is a theoretical plate. The more of these, the better the efficiency.

Ideally, the best separation should take place when the temperature offers the most transitions in and out of the phase. This happens to be between 10 and 50°C below the boiling point of the compound for a traditional open tubular capillary column.

The boiling point of these freons is quite low, so decreasing temperatures is necessary to achieve the best separation with normal capillary columns.

Related resources:

• Solvent and Temperature Considerations
• Glycerin in Biodiesel Using a High Temperature Fused Silica GC Column
• Diesel Range Organics Analysis by High Temperature GC
• GC Troubleshooting Guide
• GC Accessories Guide
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