The Basics of Vapor-Liquid Equilibrium
(Or why the Tripoli L2 tech question #30 is wrong)

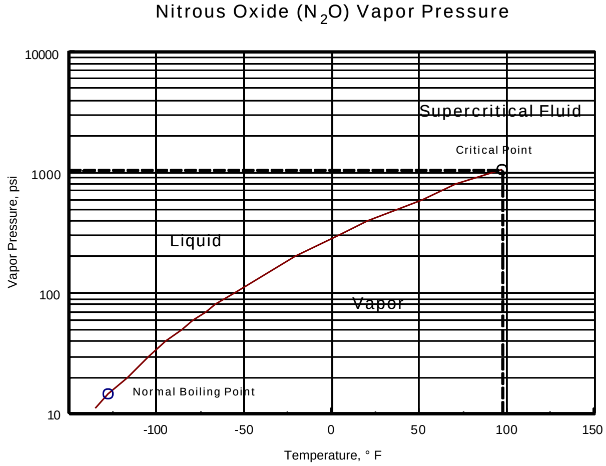
A question on the Tripoli L2 exam has the wrong answer? Yes, it does. What is this errant question?

30. Above what temperature does pressurized nitrous oxide change to a gas?
   a. 97°F
   b. 75°F
   c. 37°F

The correct answer is: d. all of the above. The answer that is considered correct, however, is: a. 97ºF. This is the critical temperature above which N_2O is neither a gas nor a liquid; it is a supercritical fluid. To understand what this means and why the correct answer is "all of the above" you have to know a little about the behavior of liquids and gases.

Most people know that water boils at 212ºF. Most people also know that when you're, for instance, boiling an egg in the mountains, you have to boil it longer to fully cook it. The reason for this has to do with the vapor pressure of water. Every liquid wants to vaporize to some extent. The measure of this tendency is known as the vapor pressure and varies as a function of temperature. When the vapor pressure of a liquid reaches the pressure above it, it boils. Until then, it evaporates until the fraction of vapor in the mixture above it is equal to the ratio of the vapor pressure to the total pressure. At that point it is said to be in equilibrium and no further liquid will evaporate. The vapor pressure of water at 212ºF is 14.696 psi – the atmospheric pressure at sea level. In the mountains, however, the atmospheric pressure is lower. At 5,000 feet, the atmospheric pressure is only about 12.2 psi. Water reaches this vapor pressure and boils at only 203ºF, so your egg-boiling water is not as hot and it consequently takes longer to cook the egg.

Okay, so now we know about vapor pressure, but what does this have to do with pressurized N_2O changing to a gas? Take a look at the following graph of the vapor pressure of N_2O versus temperature.



As you can see from this plot, the temperature at which N_2O change from a liquid to a gas is a function of the pressure it is under. For N_2O at about 500 psi, it will change from a liquid to a vapor at about 37ºF. At around 820 psi, it will boil at 75ºF and at 1050 psi, it will boil at 97ºF or so. But what about this critical point thing? What happens there? To answer this question, we first have to think about how we distinguish between a liquid and a gas.

So how **do** we distinguish a liquid from a gas? Density. When we have a vapor-liquid system at equilibrium, we have two phases present. The more dense phase is called a liquid, the less dense phase is called a vapor. As you move along the equilibrium curve towards the critical point, increasing temperature and pressure, the densities of the two phases become closer and closer to one another until, at the critical point, they become identical. There is only one phase. This can lead to some interesting effects. If I have nitrous oxide at 50ºF and 700 psi, a quick glance at the graph, above, shows that I have a liquid. Let's take this liquid and put it in a transparent cell. At this point if we lowered the pressure, at about 600 psi we'd see a bubble form and we'd be able to confirm that we did, indeed, start out with a liquid. If we took the cell and dropped the pressure to 500 psi, we'd have a vapor. If we then increased the pressure of the vapor, when we hit 600 psi, a drop of liquid would form confirming that we did, indeed, start with a vapor. Why is this important? Because by simply looking into the cell, we'd only be able to determine whether we were liquid or vapor if there was a drop or bubble present. Now the mind games begin. We take our cell at 50ºF and 700 psi and raise the pressure to 1100 psi, keeping the temperature constant. We then increase the temperature to 110ºF keeping the pressure at 1100 psi. We now drop the pressure to 500 psi and keep the temperature at 110ºF. What have we observed to far in our cell? Nothing. No change of phase from a liquid. We've actually gone from being a liquid to being a supercritical fluid and have changed the temperature of this supercritical fluid, but you've not observed any changes in the cell. Okay, now we cool the cell down to 37ºF and what happens? A drop forms. What? That must mean that we're a vapor and we're condensing liquid? But we started out with a liquid and it never boiled. Oh the joys of supercriticality.

What does this have to do with rocketry, anyway? If you're using N_2O to fly hybrids, it's critical. The N_2O liquid in a tank is at equilibrium with the vapor in the tank. This means that the tank pressure is equal to the vapor pressure of N_2O at the ambient temperature. At 75ºF, your tank pressure will be at about 800 psi. If you heat the tank to 95ºF, the pressure will rise to about 1000 psi and the amount of vapor in the tank will decrease. At and above the critical point, an equation of state appropriate for supercritical fluids must be used to calculate the tank pressure at a given temperature.

So, what should be done with the infamous question #30? To be fair, in the answer on the web site, it does refer to the N_2O as being a supercritical gas above 97ºF. But the question is not worded properly for the answer. N_2O is **not** a gas of any type above its critical point. It is a supercritical fluid. Perhaps the question should be worded "Above what temperature does NOX not exhibit a liquid and gas phase?" But I'll leave that to the experts.

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