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May 15, 2019 Karim Mahraz, Product Manager at Swagelok, Analytical Instruments While phase charts are mainly used by chemists in the laboratory, these tools can be surprisingly useful for mechanical engineers and plant managers tasked with analyzing samples. In some analytical systems, the liquid sample must be converted into gas by evaporation before it can be analyzed. Evaporation is essentially a balancing act between temperature, pressure and flow variables, and phase para pressure curves allow engineers to detect phase changes for different materials and chemical compounds. As you read further, a hypothetical gas mixture of 20% hexagon in pentana will be applied as a complete phase chart (see chart below). When the sample is above the bubble point (blue line), it will be completely in the liquid phase. The sample must remain in a liquid state when entering the vaporizer. When the sample is below the dew point (golden line), it is all steam. The sample should be all steam when it leaves the vaporizer. Between the bubble point and the dew point lines is an area without going. This zone is the boiling range of the sample. Here the mixture is in two phases: part liquid and part of steam. Once the sample falls into the non-go zone, it is fractional and no longer suitable for analysis. The purpose of evaporation is to set the temperature, flow and pressure so that the sample instantly skips from the liquid side of the zone not-go-side to steam. With clean and almost clean samples, there is virtually no boiling range or no-go zone. The point of the bubble and the dew point line is just on top of each other or almost so. Pure and almost pure specimens are converted into pairs of the same composition, whether evaporation or evaporation. Some industrial designs approach this level of purity and are transformed quite easily. On the other hand, some samples have such a wide boiling range or non-go zone that they cannot be successfully evaporated. Such samples cannot be missed from the liquid side of the non-go zone to the steam side. In this case, the variables cannot be manipulated to avoid the faction. In the diagram shown above, the strip between the bubble point and the dew point is narrow enough that, with proper settings, the sample can effectively move from the liquid side of the non-go zone to the steam side. At the same time, the group on the chart is wide enough that one cannot afford to be careless. Setting temperature, pressure and flow Continues to work with the sample on the diagram (20 percent hexagon in the pentana), inputs must be expertly installed to ensure successful evaporation. In general, the entrance requires high pressure and low temperature. Conversely, the output requires high temperature and low pressure. restrictions on how high and low these parameters can be, and not every restriction can be 1. Determine the pressure of the inputs on your vaporizer input pressure, which is fixed, is the pressure process, provided that the vaporizer is located next to the sample of the faucet. In the example of the chart, this pressure is 4 bars. Higher pressure is better because it allows the vaporizer to keep the temperature higher without boiling the incoming liquid. 2. Set the temperature of the entrances when setting moderate input air, there are two goals. First, the temperature should be low enough that when the sample enters the vaporizer, it is completely liquid. In the example of the chart, the bubble dot is 4 bar 88 degrees Celsius. To protect against fractionalation, it is best to choose a round number far enough from 88 degrees Celsius to avoid a no-go zone. The safe temperature of the example can be 80 degrees Celsius. The second goal is to keep the temperature high enough to promote a full flashing sample-ensuring only the vapor leaves the vaporizer. When the sample evaporates, the temperature drops in accordance with the laws of energy saving. The temperature of the sample should be high enough from the beginning that after the pressure drop the sample did not fall in the non-go zone. In the example of the chart, the vapor temperature after the pressure drop is 60 degrees Celsius - only on the steam side of the dew point line. 3. Install the pressure socket when setting the outlet pressure, the goal is to relieve the pressure below the dew point line. In the example of the diagram, the pressure of the socket is set to 1.5 bar. If the pressure in the socket was higher, the sample would not evaporate completely and will be crushed. 4. Set the flow flow set downstream on the valve and rotameter, not on the vaporizer. In the sampling system it is desirable to have a high flow of steam, as it quickly moves the sample to the analyzer. However, a high flow can be problematic because more heat is required to evaporate the sample. In other words, a high flow causes a greater drop in temperature during evaporation. In the example of the diagram, the purple line illustrates the drop in temperature. As the flow increases, the temperature drops sharply. Another variable influencing the temperature drop is the ability to transmit heat to the vaporizer. Some vaporizers are constructed in such a way that heat is transferred more efficiently to the sample. When the liquid sample is converted into steam and its temperature drops, it draws heat from the stainless steel surrounding it. The critical question is how effectively the vaporizer can replace heat and keep it flowing into the sample. The more heat the sample can draw, the less temperature it drops during evaporation. In some cases, it is possible for the vaporizer to be hot to the touch outside, but cold in the core inside. This is because the evaporated sample draws a large amount of heat and can't transmit enough energy to keep up. The best solution is to reduce the flow. In B The moderate drop visualized on the diagram is a product of the flow rate and the ability to transmit the vaporizer's heat. With good vaporizer quality and low flow speed, the line on the chart will become more vertical. Unfortunately, there is no easy way to calculate the exact location of the temperature drop in the phase chart, and it cannot be created by any known program. As a result, evaporation involves some approximation. Typically, keep the flow rate as low as possible without causing an unacceptable delay in the sample's journey to the analyzer. It is better to start with a low flow speed and experiment by increasing it than to start with an initially higher flow speed. For more help with analytical devices and sampling the system of excellence, using the phase chart of steam pressure curves, please contact your local sales and service center Swagelok. LOCATE YOUR SWAGELOK SALES AND SERVICE CENTER By the end of this section you will be able to: Explain the design and use of a typical phase chart Using phase charts to determine stable phases at a given temperature and pressure, and describe phase transitions as a result of changes in these properties Describe the supercritical phase of the liquid matter In the previous module, the change in equilibrium pressure of the vapor of the liquid with the temperature was described. Given the definition of boiling point, the vapor pressure areas compared to the temperature represent how the boiling point of the liquid changes with the pressure. The use of heating and cooling curves to determine the melting point (or freezing) of the substance was also described. Making such measurements at a wide range of pressures provides data that can be presented graphically in the form of a phase chart. The phase chart combines pressure areas compared to the temperature for liquid gas, solid liquid and solid gas phase of the equilibrium substance. These diagrams indicate physical states that exist under certain pressure and temperature conditions, and also provide dependence on phase temperature pressures (melting points, sublimation points, boiling points). A typical phase chart for a clean matter is shown in Figure 1. Figure 1. The physical condition of the substance and its phase temperature are graphically represented in the phase chart. To illustrate the usefulness of these sites, let's look at the phase diagram of water shown in Figure 2. Figure 2. Pressure and temperature axes on this phase diagram of water do not reach for a constant scale to illustrate several important properties. We can use a phase chart to determine the physical condition of a water sample under certain pressure and temperature conditions. For example, the pressure of 50 kPa and the temperature of 10 degrees Celsius area of the chart marked ice. ice. these conditions, water exists only as solid (ice). The pressure of 50 kPa and the temperature of 50 degrees Celsius correspond to the water region - here the water exists only as a liquid. At 25 kPa and 200 degrees Celsius, water exists only in a gaseous state. Note that the H2O phase chart does not stretch the pressure and temperature axis to illustrate a few important features described here. The B.C. curve in Figure 2 is a plot of vapor pressure compared to the temperature as described in the previous module of this chapter. This liquid vapor curve separates the liquid and gaseous areas of the phase chart and provides a boiling point at any pressure. For example, at 1.3 m the boiling point is 100 degrees Celsius. Note that the liquid vapor curve stops at 374 degrees Celsius and a pressure of 218 aces, indicating that water cannot exist as a liquid above that temperature, regardless of pressure. The physical properties of water in these conditions are intermediate between its liquid and gas phases. This unique state of matter is called supercritical fluid, a topic that will be described in the next section of this module. The hard vapor curve, marked AB in Figure 2, indicates the temperature and pressure at which ice and water vapor are in balance. These temperature pressure data pairs correspond to the sublimation or deposition points of the water. If we could zoom in on the solid gas line in Figure 2, we would see that the vapor pressure is about 0.20 kPa at 10 degrees Celsius. Thus, if you place a frozen sample in a vacuum with pressure of less than 0.20 kPa, the ice will be elevated. This is the basis for the drying freeze process, often used to preserve food, such as ice cream, shown in Figure 3. Figure 3. Freeze-dried foods such as ice cream are dehydrated by sublimation at pressure below the triple water point. (credit: "lwao"/Flickr) The solid liquid curve marked by BD shows the temperature and pressure at which ice and liquid water are in balance, which is a melting/freezing point of water. Note that this curve shows a slight negative slope (significantly exaggerated for clarity), indicating that the melting point of the water decreases slightly as the pressure increases. Water is an unusual substance in this regard, as most substances show an increase in melting point with increased pressure. This behavior is partly responsible for the movement of glaciers, as shown in Figure 4. The bottom of the glacier is under enormous pressure because of its weight, which can melt some of the ice, forming a layer of liquid water on which the glacier can slide more easily. Figure 4. Huge pressure under results in partial melting to produce a layer of water that provides lubricant to aid the glacial movement. This satellite photo advancing the edge of the Perito Moreno glacier in Argentina. (credit: NASA) The crossing point of all three curves is marked B in Figure 2. At the pressure and temperature represented by this point, all three phases of water coexist in balance. This pair of temperature pressure data is called a triple point. At pressure below the triple point, water cannot exist as a liquid, regardless of temperature. By determining the state of the water using the phase diagram for water in Figure 2, determine the state of the water at the following temperatures and pressures: a) 10 degrees Celsius and 50 kPa (b) 25 degrees Celsius and 90 kPa (c) 5 0 KC and 40 kPa (C) d) 80 k and 5 kPa (e) 10 degrees Celsius and 0.3 kPa (f) 50 degrees Celsius and 0.3 kPa solution using a phase chart for water. We can determine that the water condition at each temperature and pressure are as follows: (a) solid; Liquid; (c) Liquid; Gas; (e) Solid; F) Gas. Check your training What phase changes can go through the water as the temperature changes if the pressure is carried out at 0.3 kPa? If the pressure is at 50 kPa? At 0.3 kPa: latex text; (long-right); text/latex at 58 degrees Celsius. At 50 kPa: latex text; (long-right);text/latex at 0 degrees Celsius, (latex) text; Another example is the carbon dioxide phase scheme shown in Figure 5. The hard-liquid curve shows a positive slope, indicating that the CO2 melting point increases with pressure, as for most substances (water is a notable exception, as described earlier). Note that the triple point is well above 1 atm, which indicates that carbon dioxide cannot exist as a liquid under atmospheric pressure. Instead, cooling of gaseous carbon dioxide by 1 atm leads to its deposition in a solid state. Similarly, solid carbon dioxide does not melt at pressure 1 amm, but instead exalts to give carbonated CO2. Finally, note that the critical moment for carbon dioxide is observed at relatively modest temperature and pressure compared to water. Figure 5. Pressure and temperature axes on this carbon dioxide phase chart do not reach a constant scale to illustrate several important properties. Determining the state of carbon dioxide using the carbon dioxide phase chart shown in Figure 5, determine co2 at the following temperatures and pressures: a) 30 k and 2000 kPa (b) 60 degrees Celsius and 1000 kPa (c) 60 k and 100 kPa (d) 20 KC and 1500 kPa (e) 0 KC and 100 KP (f) 20 KC and 100 KP Solution Use phase chart for carbon dioxide provided We can determine that the co2 state at each temperature and pressure is given as follows: (a) liquid; (b) Solid; Gas; Liquid Gas; (f) Gas. Check your training To determine the phases of carbon dioxide change undergoing when its temperature changes, thus in a way is his pressure constant at 1500 KP? 500 KP? At what approximate temperatures are these phase changes taking place? 1500 kPa: latex text; (long-right); text/latex at 45 degrees Celsius, latex text; (long-right) : text/latex at 10 degrees Celsius; 500 kPa: latex text; «longrightarrow»« text/latex at 58 degrees Celsius If we change the water sample in an airtight container at 25 degrees Celsius, remove the air and allow the balance of evaporation and condensation to establish, we stay with a mixture of liquid water and water vapor under pressure of 0.03 aces. A clear line between a denser liquid and a less dense gas is clearly observed. As the temperature rises, the pressure of water vapor increases, as evidenced by the liquefied gas curve in the phase diagram of the water (Figure 2), the two-way phase of the equilibrium of liquid and gaseous phases remains. At 374 degrees Celsius, the vapor pressure has risen to 218 asms, and any further increase in temperature leads to the disappearance of the boundary between the liquid and steam phases. All water in the container is currently present in one phase, the physical properties of which are intermediate between gaseous and liquid states. This phase of matter is called a supercritical fluid, and the temperature and pressure over which this phase exists is a critical point (Figure 6). Over a critical temperature, the gas cannot be liquefied no matter how much pressure is applied. The pressure needed to liquefy the gas at a critical temperature is called critical pressure. Critical temperatures and critical pressure of some common substances are contained in Table 6. Substance Critical Temperature (K) Critical Pressure (atm) Hydrogen 33.2 12.8 nitrogen 126.0 33.5 oxygen 154.3 49.7 carbon dioxide 304.2 73.0 ammonia 405.5 111.5 sulfur dioxide 430.3 77.7 water 647.1 217.7 Table 6. Figure 6. (a) The airtight container with liquid carbon dioxide is heated below the critical point, which leads to the formation of a phase of supercritical liquid. Cooling of the supercritical liquid reduces its temperature and pressure below the critical point, which leads to the recovery of individual liquid and gas-shaped phases (c and d). Colored floats illustrate differences in density between liquid, lawn and supercritical fluid states. (credit: Mmrobin/YouTube) Watch the fluid transition to supercritical liquid for carbon dioxide. Like gas, the supercritical liquid will expand and fill the container, but its density is much greater than the typical gas density, usually close to those for liquids. Like liquids, these liquids are able to dissolve non-captivate soluble. They exhibit essentially no surface tension and very low viscosity, however, so that they can more penetrate very small holes in the solid mixture and remove the remove Components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, which is used for decaffeinated coffee, the removal of fats from potato chips, and the extraction of aroma and aroma compounds from citrus oils. It is non-toxic, relatively inexpensive, and is not considered a pollutant. Once used, CO2 can be easily recovered by reducing pressure and collecting the resulting gas. Critical carbon dioxide temperature If we shake the carbon dioxide fire extinguisher on a cool day (18 degrees Celsius), we can hear liquid CO2 sloshing around inside the cylinder. However, the same cylinder does not appear to contain liquid on a hot summer day (35 degrees Celsius). Explain these observations. Solution On a cool day, CO2 temperatures are below the critical CO2 temperature, 304 K or 31 degrees Celsius (table 6), so liquid CO2 is present in the cylinder. On a hot day, co2 temperatures exceed its critical temperature of 31 degrees Celsius. At this temperature, no pressure can thin out CO2, so there is no liquid CO2 in the fire extinguisher. Check your ammonia training can be liquefied by compression at room temperature; oxygen cannot be liquefied in these conditions. Why do these two gases exhibit different behaviors? The critical temperature of ammonia is 405.5 K, which is above room temperature. Critical oxygen temperature below room temperature; thus, oxygen cannot be liquefied at room temperature. Coffee is the second most common commodity in the world, following only oil. All over the world, people love the aroma and taste of coffee. Many of us also depend on one component of caffeine to help us get going in the morning or stay alert in the afternoon. But at the end of the day, the stimulating effect of coffee can keep you from sleeping, so you can choose to drink decaffeinated coffee in the evening. Since the early 1900s, many methods have been used for decaf coffee. They all have advantages and disadvantages, and it all depends on the physical and chemical properties of caffeine. Since caffeine is a somewhat polar molecule, it dissolves well in water, a polar fluid. However, since many of the other 400-plus compounds that promote coffee taste and flavor are also dissolved in H2O, hot water decaffeinated processes can also remove some of these compounds that adversely affect the smell and taste of decaffeinated coffee. Dichloromethane (CH2Cl2) and ethyl acetate (CH3CO2C2H5) have a similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aromatic components, and use them long time extraction and cleaning. As both of these solvents are toxic, health concerns have been raised regarding the remaining in decaffeinated coffee. Supercritical extraction of liquid using carbon dioxide is now widely used as a more efficient and environmentally friendly method of decaffeinated (Figure 7). At temperatures above 304.2 k and pressure above 7,376 kPa, CO2 is a supercritical liquid, with properties of both gas and liquid. Like gas, it penetrates deep into coffee beans; As a liquid, it effectively dissolves certain substances. Supercritical extraction of carbon dioxide from steamed coffee beans removes 97-99% caffeine, leaving the aroma and aromatic compounds of the coffee intact. Because CO2 is a gas under standard conditions, its removal from extracted coffee beans is easily carried out, as is the recovery of caffeine from the extract. Caffeine recovered from coffee beans through this process is a valuable product that can be used subsequently as an additive to other foods or medications. Figure 7. (a) Caffeine molecules have both polar and non-polar regions, making it soluble in solvents of different polarity. (b) The diagram shows a typical decaffeination process involving supercritical carbon dioxide. The temperature and pressure conditions at which the substance exists in solid, liquid and gas states are summarized in the phase chart for this substance. Phase diagrams are combined phases of three pressure temperature equilibrium curves: solid liquid, liquefied gas and solid gas. These curves are a link between phase temperature and pressure. The point of intersection of all three curves is a triple point of matter - temperature and pressure, at which all three phases are in balance. At pressure below the triple point, the substance cannot exist in a liquid state, regardless of its temperature. The term liquefied gas curve is a critical point of matter, pressure and temperature over which there can be no liquid phase. Chemical end of Exercise Chapter From Phase Chart for Water (Figure 2), determine the state of the water in: (a) 35 KC and 85 kPa (b) 15 KC and 40 kPa (c) 15 KC and 0.1 kPa (d) 75 K K and 3 kPa (e) 40 k and 0.1 kPa (f) 60 degrees Celsius and 50 kPa What phases of change will happen when water is exposed to different pressures at a constant temperature of 0.005 degrees Celsius? At 40 degrees Celsius? At 40 degrees Celsius? The pressure of the stove allows the food to cook faster because the higher pressure inside the pressure cooker increases the boiling point of the water. A special pressure cooker has a protective valve that is installed to ventilate steam if the pressure exceeds 3.4 3 3 m. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning. On the carbon dioxide phase chart 5 Determine co2 by: a) 20 degrees Celsius and 1000 kPa (b) 10 degrees Celsius and 2000 kPa (c) 10 degrees Celsius and 100 kPa (d) 40 degrees Celsius and 500 kPa (e) 80 euros and 1500 kPa (f) 80 degrees Celsius and 10 kPa identify phase changes that carbon dioxide undergoes when pressure changes if the temperature is at 50 degrees Celsius? If the temperature is at 40 degrees Celsius? At 20 degrees Celsius? (See the phase chart in Figure 5) Consider a cylinder containing a mixture of liquid carbon dioxide in balance with carbon dioxide at the initial pressure of 65 atm and a temperature of 20 degrees Celsius. A sketch of the plot depicting a change in the pressure of the cylinder over time, as carbon dioxide is released at a constant temperature. Dry ice, CO2 (s), does not melt at atmospheric pressure. The air temperature will be 78 degrees Celsius. What is the lowest pressure at which CO2 (s) will melt to give CO2 (l)? At what temperature will it happen? (See Figure 5 for the phase chart.) If a severe storm causes a loss of electricity, you may need to use a rope for dry laundry. In many parts of the country at the end of winter, clothes will quickly freeze when they hang on the line. If there's no snow, will they dry anyway? Explain your answer. Is it possible to liquefy nitrogen at room temperature (about 25 degrees Celsius)? Is it possible to thin out sulphur dioxide at room temperature? Explain your answers. Elementary carbon has one gas phase, one liquid phase and two different solid phases, as shown in the phase chart: (a) The phase chart denotes gas and liquid areas. (b) Graphite is the most stable phase of carbon under normal conditions. In the phase chart, mark the graphite phase. c) If graphite is heated to 2500 K under normal conditions, while the pressure increases to 1010 Pa, it is converted into a diamond. Diamond phase label. (d) Circle of each triple point on the phase chart. (e) At what stage is carbon at 5000 K and 108 Pa? (f) If the carbon sample temperature increases from 3,000 K to 5,000 K at a constant pressure of 106 Pa, what transition phase occurs, if any? critical point temperature and pressure over which the gas cannot be condensed into a schedule of pressure and temperature of the liquid phase, summarizing the conditions under which the phases of the substance may exist supercritical fluid matter at temperature and pressure above the critical point; Exhibits properties intermediate between those of the gaseous and liquid states of triple point temperature and pressure, in which the vapor, liquid and solid phases of the substance are in the equilibrium Of The Answers to The Chemistry End of Chapter Exercise 2. At low pressure and 0.005 degrees Celsius, water is gas. As the pressure increases to 4.6 torr, the water becomes solid; As the pressure increases even more, it becomes fluid. At 40 degrees Celsius, the water at low pressure is steam; at pressure higher than about 75 it is converted into liquid. At 40 degrees Celsius, the water goes from gas to solid, as the pressure rises above very low values. 4. (a) (a) (b) Solid; Gas; Gas; (f) Gas 6. 8. Yes, the ice will be sublime, although it may take a few days. Ice has a slight vapor pressure, and some ice molecules form a gas and run away from ice crystals. Over time, more and more solid is converted into gas until eventually the clothes are dry. 10. (a) (b) (b) (d) (d) liquid phase (f) sublimation vapor pressure curves and phase diagrams worksheet answers

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