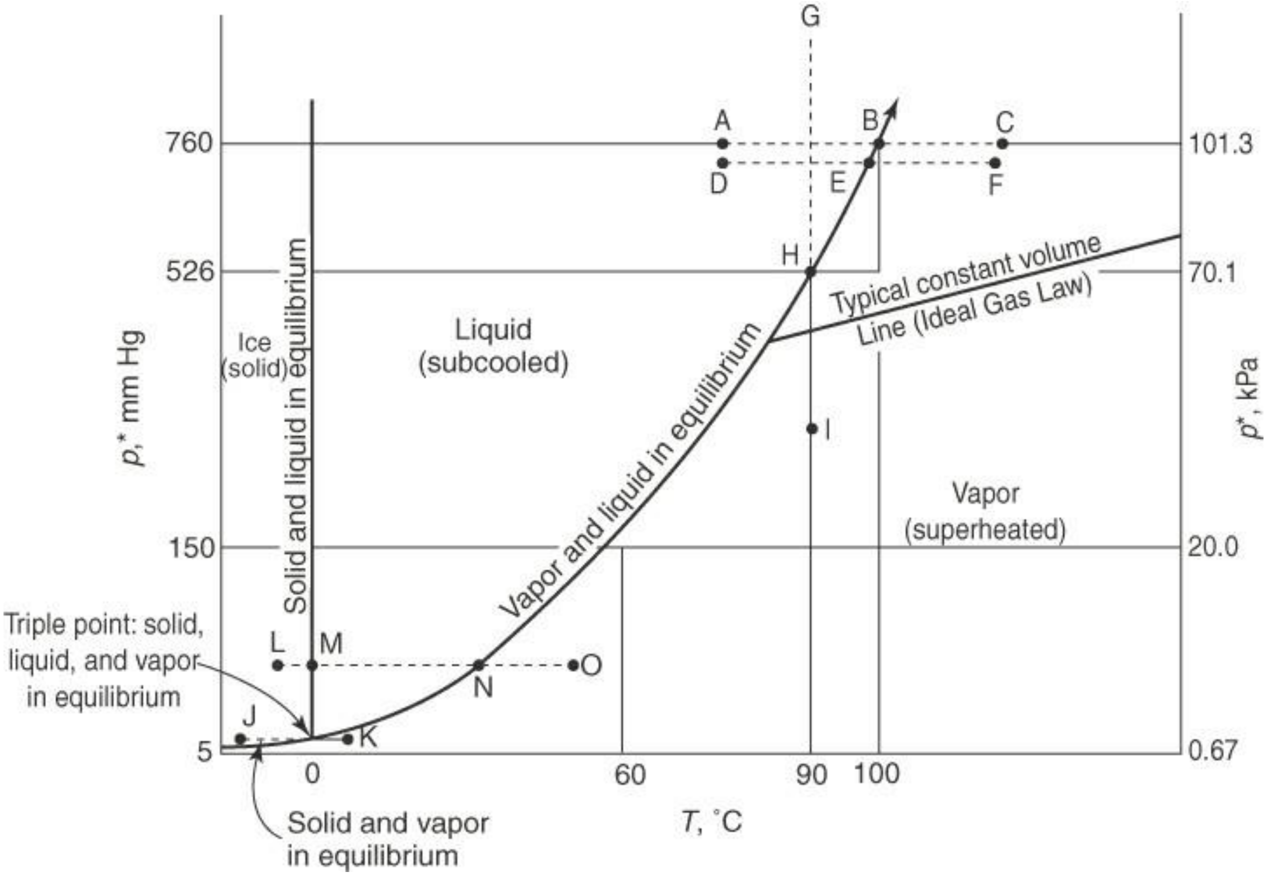
1. Phase Diagrams and the Phase Rule

If the vapor and liquid of a pure component are in **equilibrium**, the **equilibrium pressure is called the vapor pressure,** which we will denote by *p**. **At a given temperature, there is on one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium.** Either phase alone may exist, of course, over a wide range of conditions.

We next take up some terminology associated with processes that are conveniently represented on a *p*-T* phase chart such as Figure 1 (in the definitions of terms that follow, the letters in parentheses refer to the corresponding process denoted in Figure 1 by the same sequence of letters)



- **Boiling:** The change of phase from liquid to vapor (e.g., B, E, N; note that because boiling occurs at a constant temperature and pressure, the process of boiling appears as a point in a *p*-T* diagram).
- **Bubble point:** The temperature at which a liquid just starts to vaporize (N, H, and E are examples).

- **Condensation:** The change of phase from vapor to liquid (e.g., N, E, B; note that because condensation occurs at a constant temperature and pressure, the process of condensation appears as a point in a *p*-*T* diagram).
- **Dew point:** The temperature at which the vapor just begins to condense at a specified pressure, namely, temperature values on the horizontal axis read from the vapor pressure curve (N, H, and E are examples).
- **Evaporation:** The change of phase from liquid to vapor (e.g., D to F, A to C, or M to O).
- **Freezing (solidifying):** The change of phase from liquid to solid (N to L).

  Melting (fusion): The change in phase from solid to liquid (L to M; similarly to boiling, the process of melting or fusion appears as a single point in a *p*-*T* diagram).
- **Melting curve:** The solid-liquid equilibrium curve starting at the triple point and continuing almost vertically through M.
- **Normal boiling point:** The temperature at which the vapor pressure (p^*) is 1 atm (101.3 kPa) (point B for water); the temperature at which a liquid will begin to boil at the standard atmospheric pressure.
- **Normal melting point:** The temperature at which the solid melts at 1 atm (101.3 kPa).
- **Saturated liquid/saturated vapor:** Values along the liquid and vapor equilibrium curve (vapor-pressure curve, e.g., N to B).
- **Subcooled liquid:** *T* and *p* values for the liquid between the melting curve and the vapor-pressure curve (liquid D is an example).
- **Sublimation:** Change in phase from solid to vapor (J to K).
- **Sublimation curve:** The solid-vapor equilibrium curve from J (and lower) to the triple point.
- **Sublimation pressure:** The pressure along the melting curve (a function of temperature).

  Supercritical region: *p*-*T* values above the critical point (not shown in Figure 1).

  Superheated vapor: Values of vapor at temperatures and pressure exceeding those at saturation; I is an example. The **degrees of superheat** are the differences in temperature between the actual *T* and the saturated *T* at the given pressure. For example, steam at 500°F and 100 psia (the saturation temperature for 100 psia is 327.8°F) has (500 - 327.8) = 172.2°F of superheat.
- **Vaporization:** The change of phase from liquid to vapor (for example, D to F).

In Figure 1, the process of evaporation (A to C) and condensation (C to A) of water at 1 atm is represented by the line ABC with the phase transformation occurring at 100°C. Suppose that you went to the top of Pikes Peak and repeated the process of evaporation and condensation in the open air. What would happen then? The process would be the same (points DEF) except the temperature and pressure at which the water would begin to boil, or condense. Since the pressure of the atmosphere at the top of Pikes Peak is lower than 101.3

kPa, the water would start to boil at a lower temperature. Some unfortunate consequences might result if you expect to kill certain types of disease-causing bacteria by boiling the water! In addition, it will take longer to cook rice at that elevation due to the lower boiling point for water at higher elevations.

To conclude, *at equilibrium* you can see that (a) at any given temperature water exerts its unique vapor pressure; (b) as the temperature goes up, the vapor pressure goes up, and vice versa; and (c) it makes no difference whether water vaporizes into the air, into a cylinder closed by a piston, into an evacuated cylinder, or the atmosphere; at any temperature, it still exerts the same vapor pressure as long as the liquid water is in equilibrium with its vapor.

A pure compound can change phase at constant volume from a liquid to a vapor, or the reverse, via a constant temperature process as well as a constant pressure process. A process of **vaporization**, or **condensation, at constant temperature** is illustrated by the lines GHI or IHG, respectively, in Figure 1. Water would vaporize or condense at constant temperature as the pressure reached point H on the vapor-pressure curve. The change that occurs at H is the increase or decrease in the fraction of vapor, or liquid, respectively, at the fixed temperature. The pressure does not change until all of the vapor, or liquid, has completed the phase transition.

Now let's go back to the experimental apparatus and collect data to prepare $p-\hat{V}$ a phase chart. This time you want to hold the temperature in the chamber constant and adjust the volume while measuring the pressure. Start with compressed liquid water (subcooled water) rather than ice, and raise the piston so that water eventually vaporizes. Figure 2 illustrates by dashed lines the measurements for two different temperatures, T_1 and T_2. As the pressure is reduced at constant T_1, $\hat{V}$ increases very slightly (liquids are not very compressible) until the liquid.

The dots in Figure 2 represent just the measurements made when saturation of liquid and vapor occurs, and are deemed to form the envelope for the two-phase region that from a different perspective appears in Figures 1 and 2 as the vapor pressure curve. The two-phase region (e.g., A to B or D to C in Figure 2) represents the conditions under which liquid and vapor can exist at equilibrium. Note from Figure 2 that a change in the specific volume occurs in going from a liquid to a solid at the triple point.

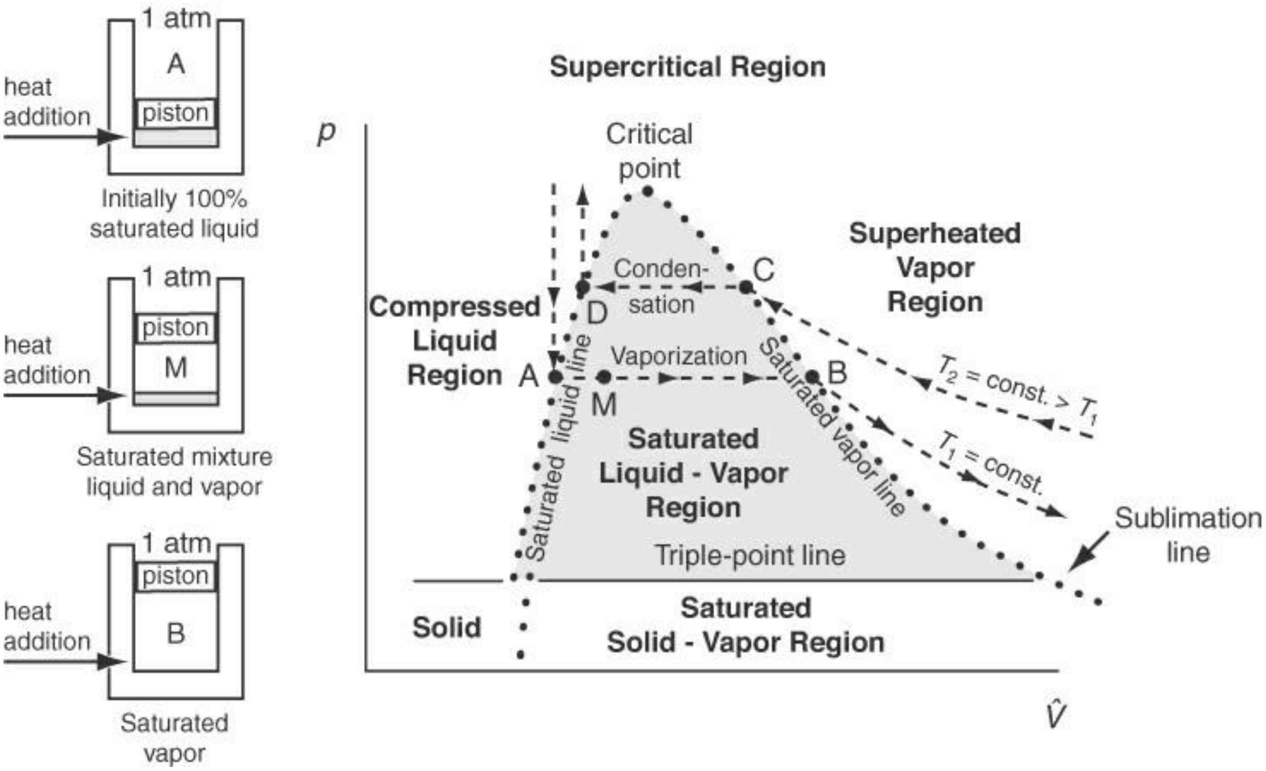


Figure 2 Experiments to obtain a $p-\hat{V}$ phase diagram. The dashed lines are measurements made at constant temperatures T_1 and T_2. The dots represent the points at which vaporization, or condensation, respectively, of the saturated liquid, or vapor, occurs; they form an envelope about the two-phase region.

Figure 2 involves a new term, **quality**, the fraction or percent of the total vapor and liquid mixture that is vapor (wet vapor). Examine Figure 3. You can calculate the volume of the liquid-vapor mixture at B in Figure 3 by adding a volume fraction of material that is saturated liquid to the volume fraction that is saturated vapor:

$$\hat{V} = (1-x)\hat{V}^{\text{sat.}}_{\text{liquid}} + x\hat{V}^{\text{sat.}}_{\text{vapor}}$$

where x is the fractional quality. Solving for x yields:

$$x = \frac{\hat{V} - \hat{V}^{\text{sat.}}_{\text{liquid}}}{\hat{V}^{\text{sat.}}_{\text{vapor}} - \hat{V}^{\text{sat.}}_{\text{liquid}}}$$

That is, by examining the location of $\hat{V}$ in relation to $\hat{V}^{\text{sat.}}_{\text{vapor}}$ and $\hat{V}^{\text{sat.}}_{\text{liquid}}$, you can determine the quality.

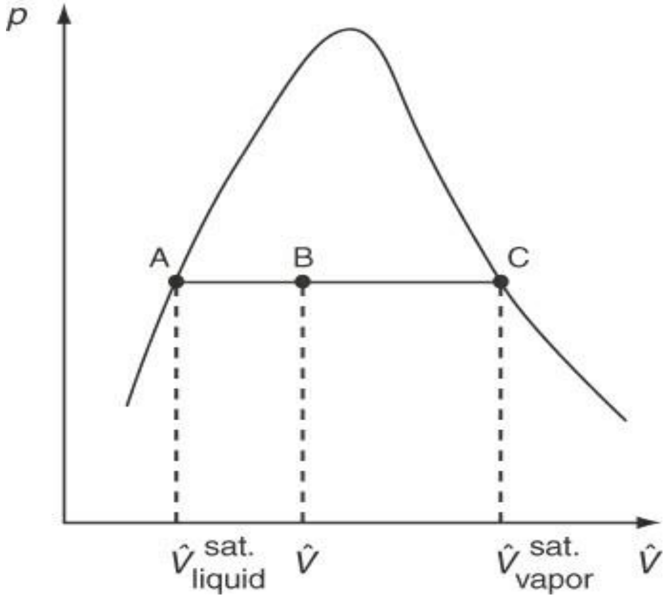


Figure 3 Representation of quality on a $p-\hat{V}$ phase diagram. A is saturated liquid, and C is saturated vapor. The compound at B is part liquid and part vapor, and the fraction vapor is called the quality.

2. Phase Rule

The phase rule is concerned only with the **intensive** properties of the system. By intensive, we mean **properties that do not depend on the quantity of material present**.? The total volume of a system is called an **extensive variable** because it depends on how much material you have; on the other hand, the **specific volume** (the volume per mass) or the **density** (mass per volume) are **intensive properties** because they are not independent of the amount of material present. You should remember that the specific (per unit mass) values are intensive properties; the total quantities are extensive properties. Furthermore, the state of a system is specified by the intensive variables, not the extensive ones.

The conclude is

- **Intensive properties** mean physical and chemical properties that do not depend on the quantity of material present as density, melting point, boiling point, specific heat capacity, conductivity, temperature, pressure, chemical properties, etc.
- **Extensive properties** mean the physical and chemical properties that depend on the quantity of material as energy, volume, mass, moles, weight, length, area.

You will find **Gibbs phase rule** to be a useful guide in establishing how many intensive properties, such as pressure and temperature, have to be specified to fix all of the remaining intensive properties and number of phases that can coexist for any physical system. **The rule can be applied only to systems in equilibrium** and is given by Equation (2), assuming that **no chemical reaction occurs:**

$$F = 2 - P + C$$

F = number of degrees of freedom (i.e., the number of independent properties that have to be specified to determine all of the intensive properties of each phase of the system of interest)—*not to be confused* with the degrees of freedom calculated in solving material balances that can involve both intensive *and* extensive variables. P = number of phases that exist in the system; a phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid. C = number of independent components (chemical species) in the system.

You will remember for a pure gas that we had to specify three of the four variables in the ideal gas equation $pV = nRT$ to be able to determine the remaining one unknown. You might conclude that $F = 3$. If we apply the phase rule, for a single phase $P = 1$ and a pure gas $C = 1$.

$$F = 2 - P + C = 2 - 1 + 1 = 2 \text{ variable to be specified}$$

How can we reconcile this apparent paradox with our previous statement? Easily! Since the phase rule is concerned with *intensive properties* only, the following are the phase rule variables to be included in the ideal gas law: Thus, the ideal gas law would be written

$$p\hat{V} = RT$$

An **invariant** system is one in which no variation of conditions is possible without one phase disappearing. a system that is composed of ice, water, and water vapor exists at only one temperature (0.01°C) and pressure (0.611 kPa), namely, along the triple-point line (a point in a p-T diagram), and represents one of the invariant states in the water system:

$$F = 2 - P + C = 2 - 3 + 1 = 0$$

With all three phases present, none of the physical conditions of p, T, or can be varied without one phase disappearing. As a corollary, if the three phases are present, the temperature, the specific volume, and so on, must always be fixed at the same values. This phenomenon is useful in calibrating thermometers and other instruments. Now let's look at some examples of the application of the phase rule.

Example 1 Application of the Phase Rule

Problem Statement

Calculate the number of degrees of freedom (how many additional intensive variables must be specified to fix the system) from the phase rule for the following materials at equilibrium:

- **a.** Pure liquid benzene
- **b.** A mixture of ice and water only
- **c.** A mixture of liquid benzene, benzene vapor, and helium gas
- **d.** A mixture of salt and water designed to achieve a specific vapor pressure

What variables might be specified in each case?

Solution

- **a.** $P = 1$, and $C = 1$; hence, $F = 2 - 1 + 1 = 2$. The temperature and pressure might be specified in the range in which benzene remains a liquid.
- **b.** $P = 2$, and $C = 1$; hence, $F = 2 - 2 + 1 = 1$. Once either the temperature or the pressure is specified, the other intensive variables are fixed.
- **c.** $P = 2$, and $C = 2$; hence, $F = 2 - 2 + 2 = 2$. A pair from temperature, pressure, or mole fraction can be specified.
- **d.** $P = 2$, and $C = 2$; hence, $F = 2 - 2 + 2 = 2$. Since a particular pressure is to be achieved, you would adjust the salt concentration and the temperature of the solution.

Note that in a and b it is likely that a vapor phase would exist in practice, increasing P by 1 and reducing F by 1.

Questions

1. Fill in the following table for water:

Number of Phases P	**Example**	**Degrees of Freedom F**	**Number of Variables That Can Be Adjusted at Equilibrium**
1	Steam		
2	Steam and water		
3	Steam, water, and ice		

2. Determine the number of degrees of freedom from the phase rule for the following systems at
   equilibrium:
   a. Liquid water, water vapor, and nitrogen
   b. Liquid water with dissolved acetone in equilibrium with their vapors
   c. $O_2(g)$, $CO(g)$, $CO_2(g)$, and $C(s)$ at high temperature.