

# Journey around a Phase Diagram

Nicholas K. Kildahl

Worcester Polytechnic Institute, Worcester, MA 01609

Phase equilibrium and phase diagrams are taught at the introductory level, usually following a discussion of the temperature dependence of the vapor pressure of a pure liquid. However, the treatment in most textbooks is cursory and gives little or no insight into the following important questions.

- Why does a phase diagram look as it does? In particular, why is there a discontinuity at the triple point, rather than a smooth joining of solid–vapor (s–v) and liquid–vapor (l–v) lines?
- What is the appearance of the system (i.e., the pure substance in an appropriate container) at various points (states) on the phase diagram?
- What happens to various properties of the system (e.g., volume, enthalpy, entropy, and moles of solid, liquid, or vapor) as processes (i.e., pressure and temperature changes) are carried out on the system?

This paper presents some ideas for dealing with these questions at the introductory level.

## The Equilibrium Vapor Pressure

### *Liquid in Equilibrium with Its Vapor*

Before phase diagrams can be introduced, students must be familiar with various aspects of the equilibrium vapor pressure. First, they must understand that the vapor pressure  $P_{\text{vap}}$  of a pure liquid increases with temperature more rapidly than linearly. There is a strong tendency for introductory students to assume that the ideal gas law governs the temperature dependence of  $P_{\text{vap}}$  and that the dependence should be linear. In fact, when one increases the temperature of a system consisting of liquid in equilibrium with its vapor,  $P_{\text{vap}}$  increases exponentially.

This may be rationalized by partitioning the vapor pressure increase into two contributions. Say that there are on average  $N_1$  molecules in the vapor phase before the temperature increase. When  $T$  is raised, the pressure due to these  $N_1$  molecules will increase linearly by the ideal gas law. However, at the higher temperature a larger fraction of molecules in the liquid phase possess the minimum kinetic energy needed to escape the potential well of the liquid, resulting in an increase in the number of molecules in the vapor phase. Say that an additional  $N_2$  molecules enter the vapor phase as  $T$  is raised. Then at the higher temperature, there will be on average  $N_1 + N_2$  molecules in the gas phase.

The total increase in  $P_{\text{vap}}$  is the result of contributions from the average number of molecules already present in the gas phase and from the additional molecules that enter the gas phase as a result of the  $T$  increase. According to this rationale,  $P_{\text{vap}}$  thus increases more rapidly than linearly. At WPI, students establish the exponential  $T$  dependence of  $P_{\text{vap}}$  in the laboratory, and discover that a plot of  $\ln P_{\text{vap}}$  vs.  $1/T$  is linear.

They are then ready to accept the Clausius–Clapeyron equation.

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{RT} + \frac{\Delta S_{\text{vap}}}{R} \quad (1)$$

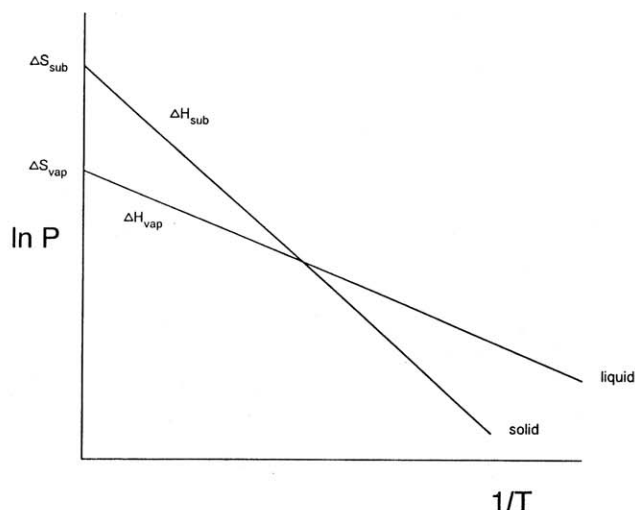


Figure 1. Clausius–Clapeyron plots for the vapor pressures of the solid and liquid phases of a pure substance.

### *Vapor in Equilibrium with a Solid*

The temperature dependence of the pressure of vapor in equilibrium with a solid is very similar to that of the vapor pressure of the liquid and is governed by the same equation. The only difference is that the enthalpy and entropy terms must be appropriate to sublimation rather than vaporization, as in the following equation.

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{sub}}}{RT} + \frac{\Delta S_{\text{sub}}}{R} \quad (2)$$

### *Comparing the Vapor Pressures of the Solid and Liquid*

A plot of  $\ln P_{\text{vap}}$  vs.  $1/T$  for both the liquid–vapor and solid–vapor equilibria on the same set of axes must have the general appearance of Figure 1. The straight line for the solid has both a more negative slope and a more positive intercept than that for the liquid. This must be true because for every substance eqs 3 and 4 hold.

$$\Delta H_{\text{sub}} > \Delta H_{\text{vap}} \quad (3)$$

(The enthalpy of sublimation implicitly contains the enthalpies of both fusion and vaporization, which are both greater than 0.)

$$\Delta S_{\text{sub}} > \Delta S_{\text{vap}} \quad (4)$$

(The solid phase is more ordered than the liquid phase.)

Because the magnitudes of both slope and intercept of the solid line must exceed those for the liquid line, the lines must cross at some temperature  $T = T_t$ . At temperatures greater than  $T_t$ , the vapor pressure of the solid is greater than that of the liquid, and solid will therefore convert to liquid in a closed system. At temperatures less than  $T_t$ , the vapor pressure of the solid is less than that of liquid, and liquid converts to solid in a closed system.

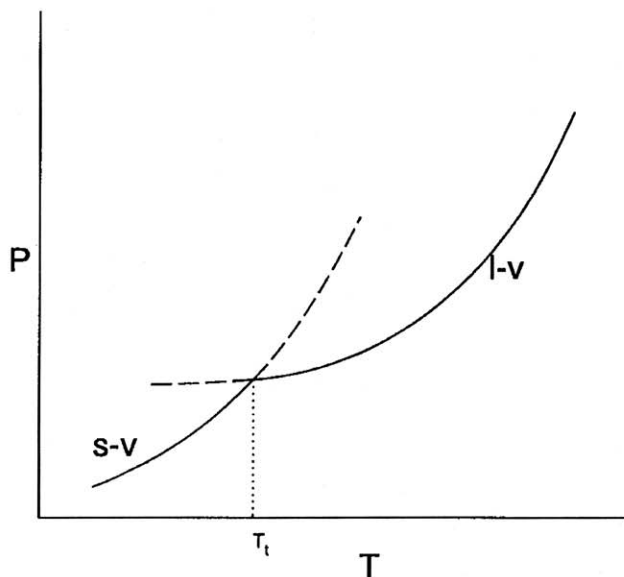


Figure 2. Vapor pressure-temperature curves for solid and liquid.

We may now translate the  $\ln P_{\text{vap}}$  vs.  $1/T$  plots for liquid and solid to  $P_{\text{vap}}$  vs.  $T$  plots, using a few simple realizations.

- Because  $\ln P_{\text{vap}}$  for the solid is less than  $\ln P_{\text{vap}}$  for the liquid at large  $1/T$  (low  $T$ ),  $P_{\text{vap}}$  for the solid is less than  $P_{\text{vap}}$  for the liquid at low  $T$ .
- Because the Clausius-Clapeyron plot for the solid has the steeper slope, the vapor pressure of the solid rises more rapidly with  $T$  than that for the liquid.
- Plots of  $P_{\text{vap}}$  vs.  $T$  for solid and liquid will not be linear, but will have upward curvature.
- These plots will cross each other at the temperature  $T_t$ .

### The Triple Point

This crossover point is the discontinuity referred to in the first question above. The result of translating the Clausius-Clapeyron plots to plots of  $P_{\text{vap}}$  vs.  $T$  is presented in Figure 2. The curve labelled l-v represents all P-T combinations at which liquid and vapor coexist in equilibrium. Similarly, the curve labelled s-v represents P-T combinations for solid-vapor equilibrium. Because the point at which these two curves intersect lies simultaneously on both curves, all three phases must coexist here. For this reason, this point is called the triple point.

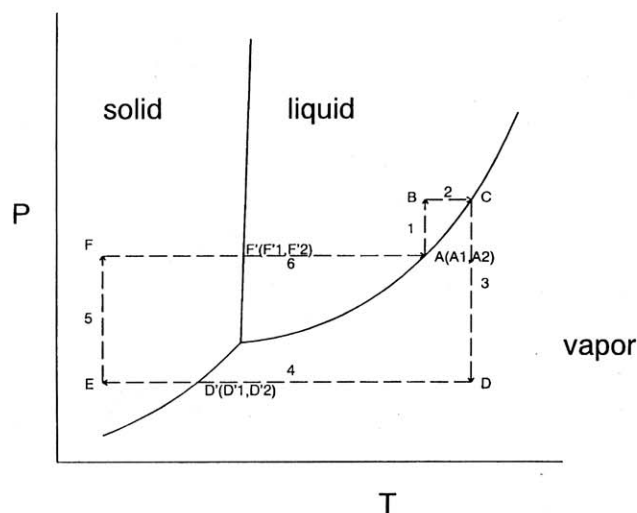


Figure 3. The phase diagram for a pure substance. Lettered points are various states of the system; numbered lines represent pathways between states.

The locus of P,T combinations at which solid and liquid coexist in equilibrium must include the triple point and slopes sharply and positively up from it. The line is steeply sloped because solid and liquid are both condensed phases, so their properties are largely pressure-insensitive. Normally, the solid phase has higher density than the liquid phase. Thus, for most substances the line has positive slope, reflecting the tendency for the substance to convert to the denser phase under increased pressure. For a few substances, water among them, liquid is denser than solid near the melting point, and increased pressure converts solid to liquid. These substances have a negatively sloped s-l line.

### The Cyclic Journey

The phase diagram for a typical pure substance is the superposition of l-v, s-v, and s-l P vs.  $T$  curves for the substance. At points on the lines, two phases exist in equilibrium. At points off the lines, only one phase exists. Figure 3 shows a phase diagram for a pure substance. It is instructive to make a cyclic "journey" around this phase diagram, to improve understanding of the changes that take place in the system as the pressure and temperature are varied.

The pure substance is considered to be in a cylinder/piston container, with no other substances present. The pressure on the system is exerted through the piston and may

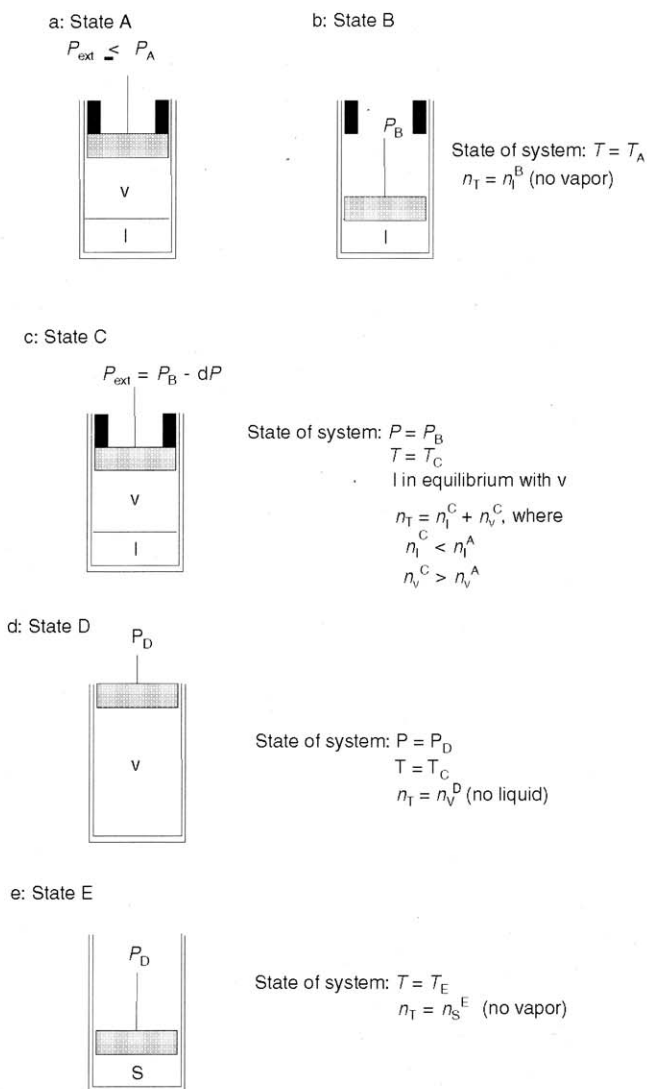


Figure 4. States of the system at various points during the journey.

be changed at will. The system temperature is maintained by immersing the cylinder in a bath at the desired  $T$ . Students should realize that phase diagrams apply only when the pure substance is contained by itself in such an apparatus.

The journey begins and ends at point A on the diagram. The system is taken by numbered paths to various lettered states and is ultimately returned to state A. The appearance and state of the system are pictured in Figure 4a. State A of the substance is characterized by pressure  $P_A$  and temperature  $T_A$ . Because point A is on the l-v line, the situation is one of liquid-vapor equilibrium. The total moles of substance in the system  $n_T$  is given by the sum of the numbers of moles of substance in the liquid and vapor phases

$$n_l^A + n_v^A$$

where the symbol  $n_l^A$  signifies the moles of substance in the liquid phase in state A. The piston rests against the mechanical stops of the cylinder because the external pressure  $P_{\text{ext}}$  is kept somewhat below  $P_A$ .

**Operation 1.** The external pressure is increased to  $P_B$ , keeping the temperature constant at  $T_A$ . What happens in the system?

All vapor condenses until only liquid exists in the cylinder because  $P_{\text{ext}}$  exceeds the value of the equilibrium vapor pressure at  $T_A$ . At  $(P, T)$  points between the s-l and l-v lines, only liquid exists in the system. The system now looks like Figure 4b.

**Operation 2.**  $P_{\text{ext}}$  is decreased by an infinitesimal amount to  $P_B - dP$ , and  $T$  is increased to  $T_C$ .

The external pressure must be decreased so that the piston will move. However, it is decreased only enough to insure this. What happens in the system? When  $T$  reaches  $T_C$ , the vapor pressure of the liquid ( $P_B = P_C$ ) exceeds  $P_{\text{ext}}$  ( $P_B - dP$ ), so liquid vaporizes and the piston expands to the stops. Thus, l-v equilibrium is reestablished at higher  $T$ . The system now looks like Figure 4c.

**Operation 3.**  $P_{\text{ext}}$  is decreased to  $P_D$ , keeping  $T$  constant at  $T_C$ . The stops are removed.

Because  $P_{\text{ext}} < P_B$ , the piston moves out. The liquid vaporizes to maintain  $P_B$  inside, and the piston continues to move out. Finally all liquid vaporizes, and the piston moves out until the internal pressure of the vapor is  $P_D$ . The piston then stops. At this point, only vapor exists in the system; only vapor can exist at the  $(P, T)$  points below the l-v line. Figure 4d shows the system.

**Operation 4.** The temperature of the system is decreased to  $T_E$ , while keeping the external pressure constant at  $P_D$ .

As soon as the temperature is lowered a little from  $T_C$ , the internal pressure falls slightly below  $P_D$ , and the piston moves in. Continued lowering of  $T$  causes the piston to move in continuously with internal  $P$  slightly less than  $P_D$ . When the temperature reaches the value at point  $D'$ ,  $T_{D'}$ , solid begins to form. The internal  $P$  remains at  $P_D$ , the temperature remains at  $T_{D'}$ , and the piston continues to move in because the amount of vapor is decreasing. When all of the vapor has deposited, temperature falls to the final value of  $T_E$ . Only solid can exist at points to the left of the s-v and s-l lines. The system now looks like Figure 4e.

The reader may wish to describe what happens in the system as a result of the last two operations indicated in Figure 3 and to draw the system diagram for states F and A.

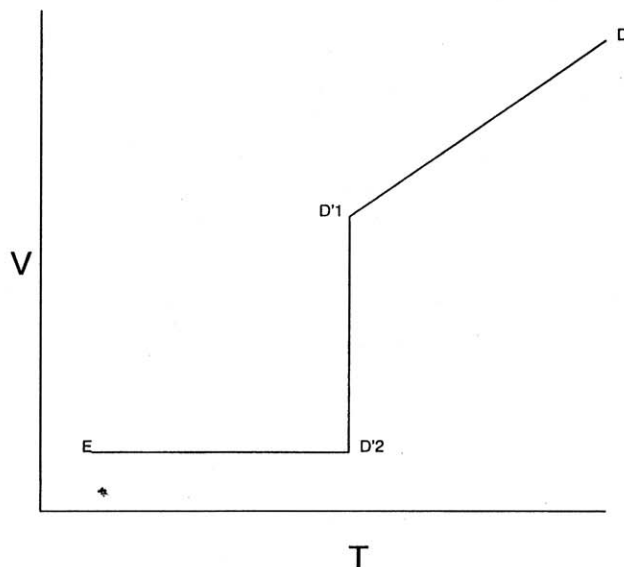


Figure 5. Volume of the system as a function of temperature for process 4 of Figure 3.

**Operation 5.** Increase  $P_{\text{ext}}$  to  $P_F$ , while keeping  $T$  constant at  $T_E$ .

**Operation 6.** Restore the cylinder stops. Increase temperature of the system to  $T_A$  keeping  $P_{\text{ext}}$  constant at  $P_F$ .

#### State Functions

##### Volume as a Function of Temperature

Additional benefit is gained by considering what happens to various state functions of the system during the numbered processes. For example, a plot of the volume of the system as a function of temperature for process 4 is shown in Figure 5. At point D, the system is entirely vapor, and the volume is relatively large. Between points D and D'1, the system is still entirely vapor, so the volume decreases linearly with temperature according to the ideal gas law. At D'1, deposition of vapor to solid begins, and the volume of the system shrinks drastically at constant temperature until all vapor is gone at point D'2. (D'1 and D'2

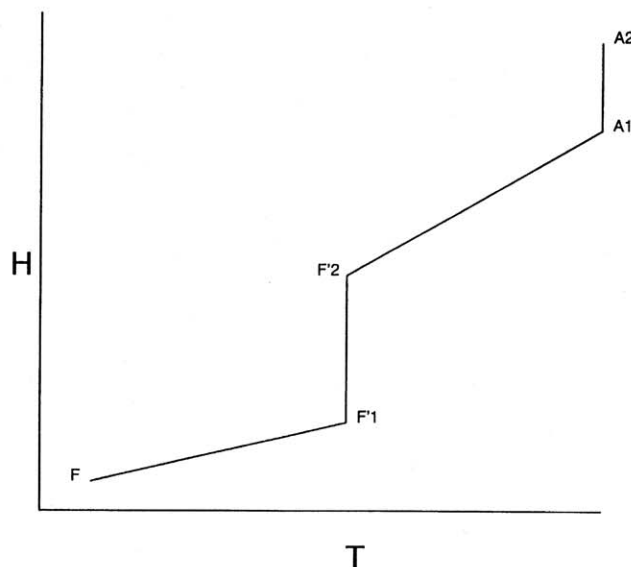


Figure 6. Enthalpy of the system as a function of temperature for process 6 of Figure 3.

are two of the many different states of the system at the pressure and temperature corresponding to point  $D'$  of Figure 3.) Further cooling of the solid from the temperature at  $D'2$  to the temperature at  $E$  results in very little further change in volume.

#### *Enthalpy as a Function of Temperature*

As a second example, a plot of the enthalpy of the system as a function of temperature for process 6 is shown in Figure 6. At point  $F$ , the system is entirely solid at a relatively low temperature, so the enthalpy is relatively low. Between points  $F$  and  $F'1$ , the solid is being heated, so the enthalpy increases linearly with slope related to the heat capacity of the solid.

At point  $F'1$ , solid begins to melt, and enthalpy increases at constant temperature until melting is complete at  $F'2$ . ( $F'1$  and  $F'2$  are two of the many states of the system at the pressure and temperature of point  $F'$  in Figure 3.) The total enthalpy change between points  $F'1$  and  $F'2$  is given by the product of the number of moles of substance and its enthalpy of fusion.

At point  $F'2$ , the system has been converted entirely to liquid. Thereafter, enthalpy increases linearly with slope related to the heat capacity of the liquid until point  $A1$  is

reached. At  $A1$ , vaporization begins and continues to point  $A2$ , where the piston hits the stops. ( $A1$  and  $A2$  are two of the many states of the system corresponding to the pressure and temperature of point  $A$  of Figure 3.) The total enthalpy rise from  $A1$  to  $A2$  depends on the amount of liquid vaporized, but is less than  $n\Delta H_{\text{vap}}^{\circ}$ .

#### *Other Plots*

Suggestions for other instructive plots are

- moles of liquid vs.  $P$  (process 3)
- moles of vapor vs.  $T$  (process 4)
- moles of liquid vs.  $T$  (process 6)
- entropy of the system vs.  $T$  (any process)

In this paper, phase diagrams have been considered in somewhat more detail than typically given in introductory textbooks of chemistry. It is hoped that these ideas will prove useful to instructors in providing insight into the phase behavior of pure substances.

#### **Acknowledgment**

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