3.D.1. Phase Diagrams

Consider a PVT system of a pure substance such as water. It is well known that water exhibits 3 phases, namely, gas (vapor, steam), liquid and solid (ice). A diagram that shows the phase space regions where these phases reside is called a phase diagram. Owing to the equation of state for each phase, the system point must lie on a 3-D manifold in the 4-D phase space (S, V, T, P). However, visual representations are limited to at most 3-D. Hence, all phase diagrams are projections.

Typical phase diagrams for a PVT system are shown in Fig.3.4-6. The variables (P, V, T) are used since they are easier to measure accurately than S. Obviously, the system point is restricted to the region with $P, V, T \geq 0$. Since the equations of state involve only the variables (P, V, T), the projection of the system point manifold onto the (P, V, T) subspace is a 2-D surface [see Fig.3.6].
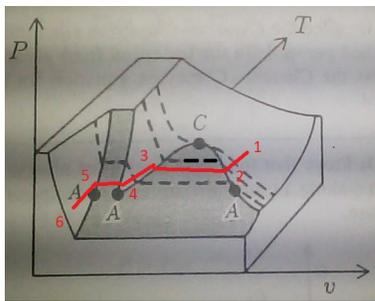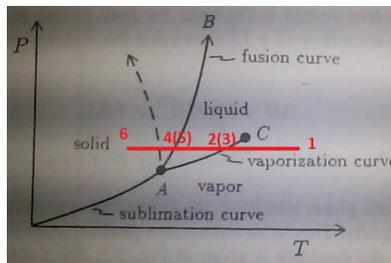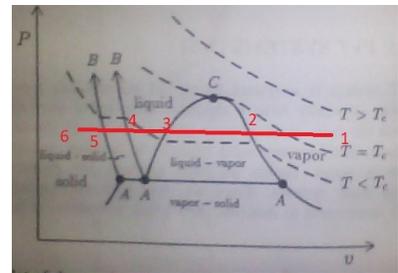

| Fig.3.6. | Fig.3.4. | Fig.3.5. |

Phase diagrams for a typical PVT system. "A" marks the triple point and "C" the critical point. Dashed lines are isotherms and red lines isobars.

It is common experience that different phases of water can coexist in arbitrary proportions at the same $P \& T$. These so called coexistence regions are represented as shaded areas in Fig.3.6. Their projections onto the T-P plane are 1-D curves called coexistence curves [see Fig.3.4]. They are named after the transition process involved. Thus, the one between gas & liquid phases is called the vaporization (or condensation) curve; that between liquid & solid phases, the fusion (or freezing) curve; and finally, that between solid & vapor phases, the sublimation (or deposition) curve.

Note that the fusion curve extends indefinitely, but the sublimation and vaporization curves end in the triple and critical point, respectively. As mentioned earlier, all phase transitions in a PVT system are 1st order, except for the 2nd order one at the critical point.

Now, there is no distinction between the vapor and liquid phases at the critical point. Furthermore, by following a path that goes around the critical point without crossing the vaporization curve, the system can change smoothly from vapor to liquid, and vice versa, without experiencing an abrupt phase transition. This is possible because the gas and liquid phases share the same spatial symmetry as described by the (continuous) Euclidean group E^3. In contrast, since the (crystalline) solid phase has the lower symmetry of some (discrete) space group, the fusion curve does not end at a critical point. All transitions between the liquid and solid phases must cross the fusion curve and suffer discontinuous changes in some system characteristics caused by the change in symmetry.

The projections of the coexistence regions onto the *V-P* plane are 2-D areas also called coexistence regions [see Fig.3.5]. Viewed as a function *V(P)*, the border of a coexistence region is multivalued.

Consider now a gas in a container equipped with a piston through which a constant pressure is maintained. By extracting heat steadily from the system, we follow the constant pressure paths (isobars) represented by red curves in the phase diagrams Fig.3.4-6. Starting at point 1 in the gas phase, we cross a family of isotherms (dashed lines) to reach a lower temperature point 2 on the coexistence (or vaporization) curve. As we enter the coexisting region, the isobar coincides with the isotherm so that the temperature remains unchanged even though heat is being extracted from the system. Meanwhile, part of the gas turns into the liquid phase so that the total volume of the system reduces continuously until point 3 on the coexistence (or condensation) curve is reached. At which point, the system is in the pure liquid phase. The heat extracted or absorbed during the crossing of the coexistence region is called the heat of condensation or vaporization, respectively. Both are examples of a latent heat, so called since no temperature change is caused by the heat transfer. Owing to the presence of this latent heat, the phase transition is classified as 1st order.

Since the gas-liquid coexistence region is reduced to a single point at the critical temperature T_C [see the $T = T_C$ isotherm in Fig.3.5], there is no latent heat involved in the phase transition, which is therefore classified as 2nd order.

As the system continues to cool down, the liquid turns into solid in the same manner, except for the absence of a critical point.

Finally, we mention that most substance possess several solid phases of different crystalline structures. Some can even condense into a glassy (amorphous) phase.