

Phase Transformation Of Pure Substances

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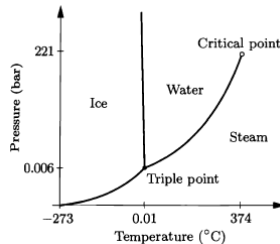
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February 11, 2021

Introduction

- A **phase transformation** is discontinuous change in the properties of a substance, as its environment is changed only infinitesimally. For instance, boiling water and melting ice. Here ice and water are called **phases**.
- Fig 1 shows **Phase diagram** of H_2O . Three regions of this diagram indicating conditions in which ice, water or steam is most stable phase. "Metastable" phases can still exist. A high pressures there are several phases of ice, with different crystal structures.

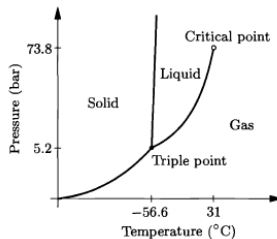


(Fig 1)

$T (^{\circ}C)$	P_v (bar)	L (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

(Fig 2)

- Lines in phase diagram represents conditions under which two different phases can coexist in equilibrium. The table in Fig 2 gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves.
- Pressure at which a gas can co-exist with its solid or liquid phase is called **vapor pressure**. Thus P_v of H_2O at room temperature is 0.03 bar.
- At $T = 0.01^\circ C$ and $P = 0.066 bar$, all three phases can co-exist; this point is called **triple point**. At lower pressures, liquid water cannot exist (in equilibrium): ice “sublimates” directly into vapor.



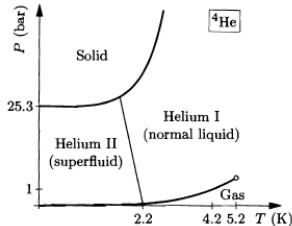
(Fig 3)

T ($^\circ C$)	P_v (bar)
-120	0.0124
-100	0.135
-80	0.889
-78.6	1.000
-60	4.11
-56.6	5.18
-40	10.07
-20	19.72
0	34.85
20	57.2
31	73.8

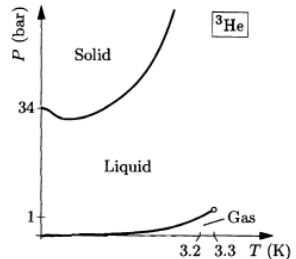
(Fig 4)

- A qualitative phase diagram for carbon dioxide is shown in Fig 3. The table shown in Fig 4 gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Sublimation of “dry ice,” frozen carbon dioxide can be seen. Evidently, the triple point of carbon dioxide lies above atmospheric pressure at 5.2 bars.
- Another difference between CO_2 and H_2O is the slope of solid-liquid phase boundary.
- A point where there is no longer any discontinuous change from liquid to gas is called the critical point, and occurs at $374^\circ C$ and 221 bars for H_2O . The critical point of carbon dioxide is at $31^\circ C$ and 74 bars.
- Close to the critical point, it's best to hedge and simply call the substance a “fluid.”
- Materials made of long molecules can, however, form a liquid crystal phase, in which the molecules move around randomly as in a liquid but still tend to be oriented parallel to each other.

- Helium has the most exotic phase behavior of any element. Fig 5 & 6 show the phase diagrams of the two isotopes of helium, the common isotope ^4He and the rare isotope ^3He .
- The boiling point of ^4He at atmospheric pressure is only 4.2K, and the critical point is only slightly higher, at 5.2 K and 2.3 bars; for ^3He these parameters are somewhat lower still. Helium is the only element that remains a liquid at absolute zero temperature.
- ^4He has two distinct liquid phases: a “normal” phase called helium I, and a **superfluid** phase, below about 2 K, called helium II.
- The superfluid phase has zero viscosity and very high thermal conductivity. Helium-3 actually has two distinct superfluid phases, but only at temperatures below 3 mK.



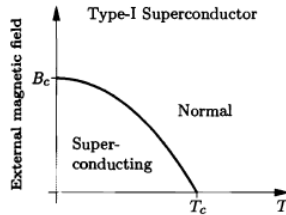
(Fig 5)



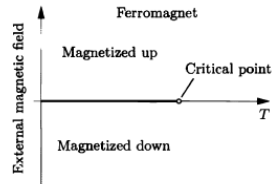
(Fig 6)

Causes of phase transformations

- Composition and magnetic field strength can also cause phase transformations. The superconducting phase, with zero electrical resistance, exists only when both the temperature and the external magnetic field strength are sufficiently low.
- Fig 7 & 8 show phase diagrams for typical **type-I superconductor**, such as lead, $T_c = 7.2K$ and $B_c = 0.08T$ & **ferromagnet** such as iron, respectively, assuming that the applied field and magnetization are always along a given axis.
- The superconducting phase, with zero electrical resistance, exists only when both the temperature and the external magnetic field strength are sufficiently low. At the **Curie temperature (1043 K for iron)**, the magnetization disappears completely, so the phase boundary ends at a critical point.



(Fig 7)



(Fig 8)

Diamonds and Graphite

- Elemental carbon has two familiar phases, diamond and graphite. At ordinary pressures the more stable phase is graphite, so diamonds will spontaneously convert to graphite, although this process is extremely slow at room temperature.
- Graphite is more stable than diamond under standard conditions is reflected in their Gibbs free energies: The Gibbs free energy of a mole of diamond is greater, by 2900 J, than the Gibbs free energy of a mole of graphite.
- But the difference of 2900 J is for standard conditions, 298 K and atmospheric pressure (1 bar). What happens at higher pressures? The pressure dependence of the Gibbs free energy is determined by the volume of the substance,

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N}$$

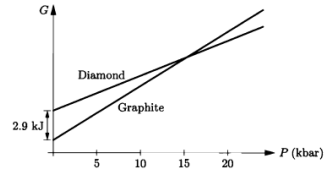
since a mole of graphite has a greater volume than a mole of diamond, its Gibbs free energy will grow more rapidly as the pressure is raised as shown in Fig 9.

- If we treat the volumes as constant, then each curve is a straight line. The slopes are $V = 5.31 \times 10^{-6} \text{ m}^3$ for graphite and $V = 3.42 \times 10^{-6} \text{ m}^3$ for diamond. As you can see, the two lines intersect at a pressure of about 15 kilobars. Above this very high pressure, diamond should be more stable than graphite.

- These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.
- The temperature dependence of the Gibbs free energies can be determined in a similar way, using the relation

$$S = \left(\frac{\partial G}{\partial t} \right)_{P,N}$$

- As the temperature is raised the Gibbs free energy of either substance decreases, but this decrease is more rapid for graphite since it has more entropy.
- Raising the temperature tends to make graphite more stable relative to diamond; the higher the temperature, the more pressure is required before diamond becomes the stable phase.
- Gibbs free energy is the key to attaining a quantitative understanding of phase transformations.



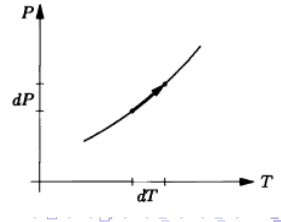
(Fig 9)

The Clausius-Clapeyron Relation

- Entropy determines the temperature dependence of the Gibbs free energy, while volume determines its pressure dependence.
- The shape of any phase boundary line on a PT diagram is related in a very simple way to the entropies and volumes of the two phases.
- Let's consider some fixed amount of the stuff, say one mole. At the phase boundary neither the liquid phase nor the gas phase is more stable, so their Gibbs free energies must be equal:

$$G_l = G_g$$

- Now imagine increasing the temperature by dT and the pressure by dP , in such a way that the two phases remain in equilibrium (see Fig.10).



(Fig 10)

- Under this change, the Gibbs free energies must remain equal, so

$$dG_i = dG_g$$

to remain on phase boundary.

- The thermodynamic identity for G

$$-S_i dT + V_i dP = -S_g dT + V_g dP$$

Now it's easy to solve for the slope of the phase boundary line, $\frac{dP}{dT}$:

$$\frac{dP}{dT} = \frac{S_g - S_i}{V_g - V_i}$$

- This results in a steep phase boundary curve, since a large pressure change is then required to compensate the small temperature change.
- On the other hand, a large difference in volume means that a small change in pressure can be significant after all, making the phase boundary curve shallower.
- It's often more convenient to write the difference in entropies, $S_g - S_i$, as $\frac{L}{T}$, where L is the latent heat for converting the material from liquid to gas. Then above equation takes the form

$$\frac{dP}{dT} = \frac{L}{T \delta V}$$

where $\delta V = V_g - V_i$. This result is known as the **Clausius-Clapeyron relation**.

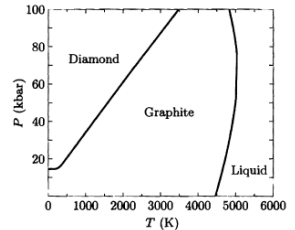
- It applies to the slope of any phase boundary line on a PT diagram, not just to the line separating liquid from gas.

Example

- Consider again the diamond-graphite system. When a mole of diamond converts to graphite its entropy increases by 3.4 J/K , while its volume increases by $1.9 \times 10^{-6} \text{ m}^3$. Therefore the slope of the diamond-graphite phase boundary is

$$\frac{dP}{dT} = \frac{\delta S}{\delta V} = \frac{3.4 \text{ J/K}}{1.9 \times 10^{-6} \text{ m}^3} = 18 \text{ bar/K}$$

- Rapid conversion of graphite to diamond requires still higher temperatures, and correspondingly higher pressures, as shown in the phase diagram in Fig 11 (The experimental phase diagram of carbon).
- In diagram, the stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure.



(Fig 11)

The van der Waals Model

- To understand phase transformations more deeply, a good approach is to introduce a specific mathematical model. For liquid-gas systems, the most famous model is the van der Waals equation,

$$(P + \frac{aN^2}{V^2})(V - N) = NkT$$

- This is a modification of the ideal gas law that takes molecular interactions into account in an approximate way.
- The van der Waals equation makes **two modifications** to the ideal gas law:
 - 1 Adding $\frac{aN^2}{V^2}$ to P.
 - 2 Subtracting N_b from V.
- The second modification is easier to understand: A fluid can't be compressed all the way down to zero volume, so we've limited the volume to a minimum value of N_b , at which the pressure goes to infinity.
- The first modification, accounts for the short-range attractive forces between molecules when they're not touching as shown in Fig 12.

- The potential energy associated with a single molecule's interactions with all its neighbors is proportional to the density of particles, or to $\frac{N}{V}$.
- The total potential energy associated with all molecules' interactions must then be

$$Total\ potential\ energy = -\frac{aN^2}{V^2}$$



(Fig 12)

- To calculate the pressure, imagine varying the volume slightly while holding the entropy fixed. Then by the thermodynamic identity, $dU = PdV$ or $P = \left(\frac{dU}{dV}\right)_S$.
- The contribution to pressure from just the potential energy is therefore

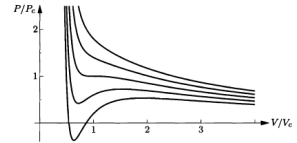
$$P_{due\ to\ p.e} = -\frac{d}{dV}\left(-\frac{aN^2}{V^2}\right) = -\frac{aN^2}{V^2}$$

- If we add this negative pressure to the pressure that the fluid would have in the absence of attractive forces (namely, $\frac{NkT}{(V-N_b)}$), we obtain the **van der Waals equation**,

$$P = \frac{NkT}{(V - N_b)} - \frac{aN^2}{V^2}$$

Consequences of the van der Waals model

- A good way to start is by plotting the predicted pressure as a function of volume for a variety of different temperatures (see Fig 13).
- At volumes much greater than N_b the isotherms are concave-up, like those of an ideal gas.



(Fig 13)

- At sufficiently high temperatures, reducing the volume causes the pressure to rise smoothly, eventually approaching infinity as the volume goes to $N - b$. At lower temperatures, however, the behavior is much more complicated.
- Real fluids don't behave like this. But a more careful analysis shows that the van der Waals model doesn't predict this.
- At a given temperature and pressure, the true equilibrium state of a system is determined by its Gibbs free energy.

- Let's start with the thermodynamic identity for G:

$$dG = -SdT + VdP + \mu dN$$

- For a fixed amount of material at a given, fixed temperature, this equation reduces to $dG = VdP$. Dividing both sides by dV then gives

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}$$

- The right-hand side can be computed directly from the van der Waals equation, yielding

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V - Nb)^2} + \frac{aN^2}{V^2}$$

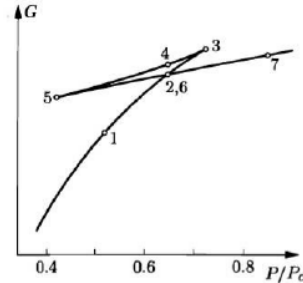
- To integrate the right-hand side, write the V in the numerator of the first term as $(V - Nb) + Nb$, then integrate each of these two pieces separately. The result is

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$$

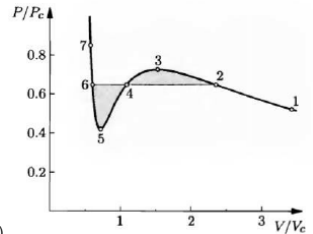
- where the integration constant, $c(T)$, can be different for different temperatures but is unimportant for our purposes. This equation allows us to plot the Gibbs free energy for any fixed T .

- Fig 14 and 15 show an example, for the temperature whose isotherm is shown alongside.
- Although the van der Waals equation associates some pressures with more than one volume, the thermodynamically stable state is that with the lowest Gibbs free energy; thus the triangular loop in the graph of G (points 2-3-4-5-6) corresponds to unstable states.
- The curved portion of the isotherm that is cut off by this straight line correctly indicates what the allowed states would be if the fluid were homogeneous; but these homogeneous states are unstable.
- since there is always another state (gas or liquid) at the same pressure with a lower Gibbs free energy. The corresponding isotherm is shown in Fig 15

$$0 = \int_{loop} dG = \int_{loop} \left(\frac{\partial G}{\partial P} \right)_T dP = \int_{loop} V dP$$

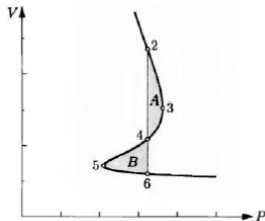


(Fig 14)

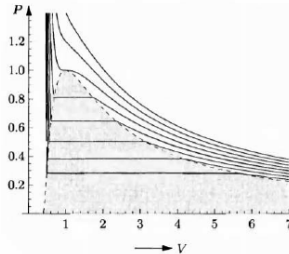


(Fig 15)

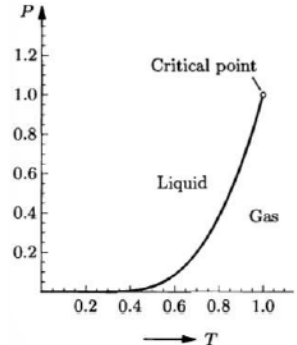
- The integral can be computed from the PV diagram, though it's easier to turn the diagram sideways (see Fig 16).
- Repeating the Maxwell construction for a variety of temperatures yields the results shown in Fig 17.
- For each temperature there is a well-defined pressure, called the **vapor pressure**, at which the liquid-gas transformation takes place; plotting this pressure vs. temperature gives us a prediction for the entire liquid-gas phase boundary.
- The straight segments of the isotherms on the PV diagram fill a region in which the stable state is a combination of gas and liquid, indicated by the shaded area.



(Fig 16)



(Fig 17)



(Fig 18)