

II.6 Application: Phase Transition

Reading assignment: S14D, R8.5-8.6, F15, F18-19

Class schedule: March 10, 12

A dilute gas described by Van der Waals equation, such as water vapor, is gradually compressed isothermally. Initially the gas may be compressed at a low pressure with a high compressibility. When the volume becomes very small, the compressibility of the substance becomes small. In both regimes, the pressure increases monotonically with the decreasing volume. When the temperature is sufficiently low, between these two regimes of low and high compressibilities, there is a regime of phase transition, and the two regimes represent two phases (gas and liquid) of the substance. When the temperature is above the critical temperature, the transition between the two phases disappears, and the substance is similar to an ideal gas dominated by thermal energy.

When the phase transition proceeds in a phase equilibrium, two phases co-exist at the constant pressure, the phase equilibrium pressure at a given temperature. Alternatively, at a given pressure, the phase equilibrium temperature is the boiling point of a liquid. In the same way, the melting point of a solid is also dependent on the pressure.

Example 1: the boiling point of water at sea level and at high altitude.

According to the second law of maximum entropy of the combined system of the two phases, the chemical potentials of the two phases are identical at the equilibrium temperature and pressure. The chemical potential of a substance is derived as a function of T and P by $N_a d\mu = -s dT + v dP$, where s and v correspond to molar entropy and volume. The phase equilibrium condition $d\mu_1 = d\mu_2$ leads to $(v_1 - v_2)dP = (s_1 - s_2)dT = \frac{L}{T}dT$, where subscript 1 and 2 describe gas and liquid phases respectively. L is the molar latent heat that is absorbed by the system to overcome the cohesive force between liquid molecules so that liquid evaporates into gas.

Example 2: the phase diagram (P-T plot) for liquid-gas transition, if the volume of the liquid is ignored.

Example 3: the melting point of ice and iron; the liquid iron core of Earth.

Remark: for most substances, the boiling point and melting point both increase with increasing pressure, i.e., $dP/dT > 0$. However, since ice water has a larger molar volume than liquid water, the melting point of ice water decreases with increasing pressure (see your HW problems).

Example 3: the phase diagram of 3 phases of water and the triple point.