Clausius-Clapeyron Equation Encyclopedia Article

Clausius-Clapeyron Equation

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Clausius-Clapeyron Equation

According to the second law of **thermodynamics**, all Carnot engines operated between two given temperatures will have the same efficiency. A Carnot cycle, then, is any reversible cycle having two adiabatic (no **heat** added) transitions and two isothermal (no **temperature** change) transitions. If we assume that an engine works between two temperatures that differ greatly and that our working substance can undergo a phase change, then the slope of the **equilibrium** lines in a pressure-temperature diagram is the Clausius-Clapeyron equation.

Examining the Carnot cycle, we can get a clearer understanding of the above assertion. The engine contains a liquid and vapor (such as water and steam) in equilibrium at temperature (T) and **pressure** (p). The specific volume of the liquid is V and the specific volume of the vapor is V. The first stage (from a to b in the figure below) is to undergo an isothermal expansion at temperature (T) and pressure (p) until a **mass** (m) has vaporized. The heat, Q, absorbed by the system in this step is the product of the mass converted and the latent **heat of vaporization** of the mass:

$Q = mL$

In the next stage (from b to c), the system expands adiabatically, i.e., it absorbs no heat, until the cylinder is at a new temperature, T and new pressure p. An isothermal compression is carried out in the third stage, maintaining T and p. The final stage in another adiabatic process to bring the system back to point a at temperature (T) and pressure (p).

Knowing that the efficiency of such an engine is:

and assuming the volume changes during the adiabatic processes are small (and so can be neglected), then

Substituting for work and solving for the ratio of the change in pressure and temp, we find:

Now, if make the assumption that the volume on the vapor is much greater that the volume of the liquid, and that it behaves as an ideal gas, this reduces to:

Knowing that L = H and

the equation becomes:

An integration over p gives us

which is the Clausius-Clapeyron equation. Comparing this equation to y=mx+b, the equation for a straight line, we see that y corresponds to ln (p) and x corresponds to 1/T. Thus, the term H/nR must be the slope of the line. Using these facts, we can glean a

variety of data from the equation; we can calculate H just given a pressure and two temperatures and so forth.