A&OS 101 The Clausius-Clapeyron equation

Winter, 2008 – Fovell

The Clausius-Clapeyron (C-C) equation can be thought of in terms of the Carnot cycle applied to a water vapor/liquid mixture. The system consists of a plunger-equipped piston filled with vapor and liquid in equilibrium (i.e., at saturation). Two adiabatic and two isothermal steps are performed. The isothermal steps involve changes of phase. The system is *not isolated* with respect to energy transfer – the phase changes will require heat exchange with the environment outside of the piston – but the total mass of water substance is conserved.

The figure below sketches a cyclic path on a diagram of saturation vapor pressure and volume. Here, volume refers to the total space occupied by the vapor/liquid mixture in the piston. We presume to know that the saturation vapor pressure is a function only of temperature. Thus, the vertical axis is really temperature. The C-C equation demonstrates this is an exponential relationship.

In this cycle, the adiabatic steps involve compression and expansion that push the system out of equilibrium, into a state of subsaturation or supersaturation, and the isothermal steps are the adjustments back to saturation. Suppose we start at A with the saturated mixture occupying volume V_A with vapor pressure e_{SA}. If we squeeze the volume a little, down to volume V_B, the temperature should go up owing to adiabatic compression. This would make the initially saturated state subsaturated, since the temperature (and thus the saturation vapor pressure) increases.
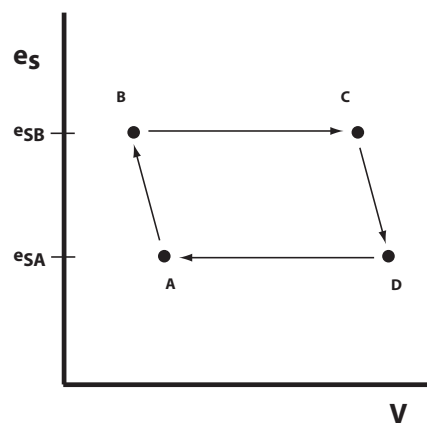

Figure 1: Conceptual e_s-V diagram for the vapor/liquid Carnot cycle. *Not to scale*. Variation on vertical axis (effectively temperature) is small; volume variation is huge.

So, some liquid has to evaporate for the system to regain equilibrium. During this process, which takes place at constant temperature and saturation vapor pressure, high density (small

volume) liquid is being replaced by low density vapor. Thus, even though we put the system out of saturation by squeezing it, regaining saturation at a higher temperature requires the volume of the system to get larger, to value V_C. The path from B to C on the figure represents the adjustment back to the saturation conditions represented by C.

Evaporation is a cooling process – for the environment hosting the system. Energy input is required to break bonds among the water molecules to permit the creation of vapor. The heat required enters the system from outside of the piston, so step B to C involves heat input Q_{IN}.

Now, disturb the equilibrium at C via adiabatic expansion. The temperature and saturation vapor pressure decrease back to the original values, and the volume increases to V_D. As the system is cooler, it is now supersaturated, and step D to A accomplishes conversion of excess vapor to liquid. During this step, low density vapor is replaced by high density liquid, and volume regains value V_A. This process is again isothermal, without change of saturation vapor pressure. Condensation warming is lost to the environment, Q_{OUT}. As in the Carnot derivation, we take the magnitudes of these two heats to be positive.

If this process is reversible (and phase changes are), the required entropy conservation is
$$\frac{Q_{IN}}{T_B} = \frac{Q_{OUT}}{T_D}.$$
We know two things: First, for the Carnot cycle, $W = Q_{IN} - Q_{OUT}$. Thus, we can write
$$W = Q_{IN}\left[\frac{T_B - T_D}{T_B}\right] = \frac{Q_{IN}}{T_B}\Delta T.$$
Second, we know that work $W = \oint p\,dV$ is also the area on a pressure-volume diagram such as shown above. The area of a parallelogram is the base times the height, or
$$W = (V_D - V_A)(e_{SB} - e_{SA}) = (V_D - V_A)\Delta e_s.$$
These two expressions for work are equivalent, so equate them. We can get
$$\frac{Q_{IN}}{T_B}\Delta T = (V_D - V_A)\Delta e_s,$$
which after rearranging and writing in differential form is
$$\frac{de_s}{dT} = \frac{Q_{IN}}{T_B(V_D - V_A)}.$$

Time to simplify. Suppose we have a unit mass system (total water 1 kg). Further suppose state D represents virtually all vapor and state A almost all liquid. Owing to the far lower density of vapor, $V_D >> V_A$, so we can neglect V_A. Q_{IN} will be equal to L_v, the latent heat of vaporization. The ideal gas law for vapor for a unit mass is $e_s V_D = R_v T_D$, but $T_D \approx T_B$ and thus we can write the C-C equation more generically as:
$$\frac{d\ln e_s}{dT} = \frac{L_v}{R_v T^2}.$$