The Second Law and evaporation of liquid

The second law of thermodynamics can be expressed in many ways, many of which can seem very confusing and unintuitive. Perhaps the easiest way to think of the second law, however, is one that is very familiar to meteorologists: matter flows from a region of high pressure to a region of low pressure. If there is no further energy added to the system, the amount of matter that is at low pressure will increase while the amount of matter that is at high pressure will decrease. Eventually, all matter will have the something close to the same (low) pressure. At this point, everything is in equilibrium.

Think about how the atmospheric circulation works. Winds (matter) blows from regions of high to low pressure. If there were no sunlight to heat the Earth, eventually everywhere on the Earth would have the same pressure. But there is sunlight, that drives the atmospheric circulations by heating and creating temperature contrasts.

Why does this matter for cloud physics? Because evaporation and condensation is like the wind, in that it too is a flow of matter from high to low pressure. We will need to consider the details of this physics more closely in order to understand why clouds form. Let’s define the Gibbs free energy (or energy that is available to do thermodynamic work) as

$$G = N\mu$$

where $\mu$ is the number of molecules, each with potential energy $\mu$. Expressed per unit material changes in $\mu$ are given by

$$\frac{d\mu}{dt} = -s\left(\frac{\partial T}{\partial t}\right)_s + v\left(\frac{\partial p}{\partial t}\right)_\alpha$$

where $s$ and $v = 1/n$ are the specific entropies and volumes and $T$ is temperature and $p$ is pressure. If both pressure and temperature are fixed then

$$\left(\frac{\partial \mu}{\partial t}\right)_{T,p} = 0$$
If just temperature is fixed then

\[
\left( \frac{\partial \mu}{\partial t} \right)_{T} = v \left( \frac{\partial p}{\partial t} \right)_{T}
\]  

(2)

Noting that at const. T, the ideal gas law take the form \( pdv + vdp = kdT = 0 \)

\[
\left( \frac{\partial \mu}{\partial t} \right)_{T} = v \left( \frac{\partial p}{\partial t} \right)_{T} = \frac{1}{n} \left( \frac{\partial p}{\partial t} \right)_{T} = -p \left( \frac{\partial v}{\partial t} \right)_{T} = - \left( \frac{\partial w}{\partial t} \right)_{T} = kT \frac{d \ln p}{dt} = -kT \frac{d \ln v}{dt} = kT \frac{d \ln n}{dt}
\]  

(3)

If we are at constant temperature (i.e. no heating), then the chemical potential energy goes down when work is done by way of expansion and a drop of pressure. Effectively \( \Delta \mu = \int_{0}^{t} \left( \frac{\partial \mu}{\partial t} \right)_{T} \ dt \) is the potential energy available per unit material that is available to do \( pdv \) work in time \( \Delta t \). Note that \( \Delta \mu \) will decline as the volume expands and potential energy is consumed.

For spontaneous processes, the second law requires that

\[
\frac{dG}{dt} = \frac{d}{dt} \left( N \mu \right) < 0
\]

Now, just because, in total, \( G \) must decrease, this does not mean that there cannot be an increase in the total potential \( G \) along any given specific potential \( \mu \). As things flow downwhill, there could be net convergence of matter at any given level. At constant \( T,p \)

\[
\left( \frac{\partial G}{\partial t} \right)_{T,p} = \mu (T,p) \left( \frac{\partial N}{\partial t} \right)_{T,p}
\]  

(4)

What we have now is the result that the extensive variable \( G \) can increase due to net convergence of material into a surface at constant temperature and pressure. If we had relaxed the pressure constraint, we could have combined Eqs. 3 and 4 to get

\[
\frac{dG}{dt} = \mu (T,p) \left( \frac{\partial N}{\partial t} \right)_{T,p} + N \left( \frac{\partial \mu}{\partial t} \right)_{N}
\]

All the above is saying is that, at constant temperature, the total potential can change either by adding more material to a particular level, or by taking the material you have and moving it to a
different level. For all potential levels $\mu_i$, this expression can be written as

$$\frac{dG}{dt} = \frac{d}{dt} \left( \sum_i \mu_i N_i \right) < 0$$

Indicating that there may be many different types of energy $\mu_i$ that come into play (e.g. gravity or latent heat), or different potential levels (e.g. heights), or different types of matter $N_i$ (e.g. photons, water vapor, air, etc...).

We’ll now do a series of problems showing how the above principles can be applied to understand the evaporation and condensation of water

1. Show that over a plane surface of pure water at constant temperature, where $RH$ is the relative humidity, that the difference in the chemical potential $\mu$ between the vapor and liquid phase is

$$\Delta \mu = \mu_v(T) - \mu_l(T) = kT \ln \left( \frac{RH}{100} \right)$$  \hspace{1cm} (5)$$

where

$$\Delta G = m \Delta g \equiv N \Delta \mu$$

where $N$ refers to the amount of matter (typically molecules) and $\Delta \mu$ is the amount of potential energy per molecule. The trick in the above is recognizing that, just above the liquid surface, vapor is in saturation (or equilibrium), such that its pressure is the same as the liquid water beneath it and $\Delta p$. Consequently, moving a vapor molecule from just above the liquid surface to the air above it is equivalent to moving it from the liquid phase to the vapor phase.

*Essentially this transfer is an example of the isothermal expansion (or compression) of an ideal gas as it goes from saturation to $RH$, where the gas we are interested in is water vapor. We are interested in the change of potential energy per molecule as it undergoes this transition. From the above*

$$\Delta G = N \Delta \mu$$
Using the symbol \( e \) for vapor pressure and noting that \( e = nkT \)

\[
\Delta \mu = \frac{1}{n} \Delta e = kT \frac{\Delta e}{e} \approx kT d \ln e
\]

The change in chemical potential required to move a vapor molecule from right at the liquid surface to some distance farther away phase is thus

\[
\Delta \mu = \mu_v - \mu_{v}^{sat} = kT \ln \frac{e}{e_{sat}} = kT \ln \frac{RH}{100}
\]

The value \( \mu_{v}^{sat} \) refers to the chemical potential of water vapor at saturation where it is in equilibrium with the liquid phase and \( \mu_{v}^{sat} = \mu_l \).

2. On the basis of the above, why does a puddle evaporate in dry conditions? Note that a system always work towards equilibrium. In this case a system always works towards a state where \( p_v = p_l \). Hint: the chemical potential of vapor molecules just above a flat surface is what the chemical potential would be at saturation. Draw a box around the vapor and liquid system, and do an accounting of the total gibbs free energy in the box for the transfer of molecules, with their respective chemical potentials \( \mu \), from the liquid phase to the vapor phase.

Consider a volume that contains dry air and liquid. The liquid potential is

\[
G_l = N_l \mu_{l}^{sat}
\]

In the rest of the volume

\[
G_v = N_v \mu_v
\]

The total potential is

\[
G = N_v \mu_v + N_l \mu_{l}^{sat}
\]

At constant temperature

\[
\frac{dG}{dt} = \frac{dN_v}{dt} \mu_v + \frac{dN_l}{dt} \mu_{l}^{sat}
\]
But molecules are neither created or destroyed so, in a close system, what leaves the surface adds to the rest of the volume (and vice versa)

\[ \frac{dN_l}{dt} = -\frac{dN_v}{dt} \]

So

\[ \frac{dG}{dt} = \frac{dN_v}{dt} \left( \mu_v - \mu_{v, \text{sat}} \right) = \frac{dN_v}{dt} \Delta \mu = \frac{dN_v}{dt} kT \ln \frac{e}{e_s} \]  \hspace{1cm} (6)

Since \( \frac{dG}{dt} < 0 \) (Eq. ??) through the second law, if \( e < e_{\text{sat}} \) then \( \Delta \mu = kT \ln \frac{e}{e_s} < 0 \) and \( \frac{dN_v}{dt} \) must be positive (i.e. evaporation). Likewise, if \( e > e_{\text{sat}} \), then \( \Delta \mu = kT \ln \frac{e}{e_s} > 0 \) and \( \frac{dN_v}{dt} \) must be negative (i.e. condensation).

3. It is often stated that the air can hold more water on a warm day. Comment

The amount of water vapor has nothing to do with the air itself, only the temperature, according to Clausius-Clapeyron.