Clausius Clapeyron Equation

The Clausius Clapeyron equation defines the vapor pressure of a gas that is in equilibrium with a liquid or solid of the same material. The equation is general and in atmospheric sciences it usually is used for water. Equilibrium in this case means the number of molecules leaving the liquid (or solid) surface and moving into the vapor state is equal to the number of gas molecules striking the liquid (or solid) surface and condensing from the vapor state to the liquid (or solid) state.

This quiliebrium can be understood using the concept of maximum entropy and in particular the the change in entropy of a system when a molecule changes state from vapor to condensed state or visa versa.

The explanation given below largely follows from Kittel: Thermal Physics (1969).

Chemical potential

Chemical potential comes from the concept of two systems in ***diffusive contact*** such that they can exchange constituents across a permeable boundary. The chemical potential, μ, of a system is defined by

$$-\frac{\mu}{k_B T} \equiv \frac{1}{g}\left(\frac{\partial g}{\partial N}\right)_U \equiv \left(\frac{\partial \sigma}{\partial N}\right)_U \tag{1}$$

$$-\frac{\mu}{T} \equiv \left(\frac{\partial S}{\partial N}\right)_U \tag{2}$$

where g is the number of accessible states, σ is the entropy, N is the number of molecules or particles in the system and U is the total energy of the system. The chemical potential has units of energy per molecule. It tells us how the entropy of a system changes when a molecule is added to the system.

Phase equilibria

The thermodynamic conditions for the coexistence of two phases such as a liquid and a gas are the conditions for the ***equilibrium*** of two systems that are in thermal, diffusive and mechanical contact. These conditions are that

$$T_l = T_g; \qquad \mu_l = \mu_g; \qquad p_l = p_g. \tag{3}$$

where T is temperature, μ is chemical potential, p is pressure, and the subscripts, l and g stand for liquid and gas respectively.

For two gases in equilibrium, the temperature and pressure would be in equilibrium. Two systems that can exchange energy and particles are in equilibrium when the temperatures, pressures and the chemical potentials are equal. From the equality of the chemical potential of the gas and liquid phases, we have

$$\mu_g(p_0, T_0) = \mu_l(p_0, T_0) \tag{4}$$

and

$$\mu_g(p_0 + dp, T_0 + dT) = \mu_l(p_0 + dp, T_0 + dT) \tag{5}$$

From the second equation we can say that

$$\mu_g(p_0,T_0)+\left(\frac{\partial\mu_g}{\partial p}\right)_T dp+\left(\frac{\partial\mu_g}{\partial T}\right)_p dT+\ldots=\mu_l(p_0,T_0)+\left(\frac{\partial\mu_l}{\partial p}\right)_T dp+\left(\frac{\partial\mu_l}{\partial T}\right)_p dT+\ldots \tag{6}$$

where the … refers to higher order terms. We subtract off (4) and keep the first order terms to get

$$\left(\frac{\partial\mu_g}{\partial p}\right)_T dp+\left(\frac{\partial\mu_g}{\partial T}\right)_p dT=\left(\frac{\partial\mu_l}{\partial p}\right)_T dp+\left(\frac{\partial\mu_l}{\partial T}\right)_p dT \tag{7}$$

We gather the *dp* and *dT* terms

$$\left[\left(\frac{\partial\mu_g}{\partial p}\right)_T-\left(\frac{\partial\mu_l}{\partial p}\right)_T\right]dp=\left[\left(\frac{\partial\mu_l}{\partial T}\right)_p-\left(\frac{\partial\mu_g}{\partial T}\right)_p\right]dT \tag{8}$$

$$\frac{dp}{dT}=\frac{\left[\left(\frac{\partial\mu_l}{\partial T}\right)_p-\left(\frac{\partial\mu_g}{\partial T}\right)_p\right]}{\left[\left(\frac{\partial\mu_g}{\partial p}\right)_T-\left(\frac{\partial\mu_l}{\partial p}\right)_T\right]} \tag{9}$$

which is the differential equation of the vapor pressure equilibrium curve.

We will now use the Gibbs free energy, *G*, to determine these partial derivatives. The Gibbs free energy is defined as

$$G\equiv U-TS+pV \tag{10}$$

The derivative of *G* is

$$dG\equiv dU-TdS-SdT+pdV+Vdp \tag{11}$$

The thermodynamic identity on conservation of energy that we have used previously generalized to include the energy associated with adding molecules to the system is

$$dQ=TdS=dU-\mu dN+pdV \tag{12}$$

Substituting this equation for *TdS* into the derivative of *G* yields

$$dG\equiv dU-dU+\mu dN-pdV-SdT+pdV+Vdp=\mu dN-SdT+Vdp \tag{13}$$

but the derivative of G is composed of the sum of the partial derivatives

$$dG\equiv\left(\frac{\partial G}{\partial N}\right)_{T,p}dN+\left(\frac{\partial G}{\partial T}\right)_{N,p}dT+\left(\frac{\partial G}{\partial p}\right)_{T,N}dp \tag{14}$$

By comparing the last 2 equations we see that

$$\left(\frac{\partial G}{\partial N}\right)_{T,p}=\mu \qquad \left(\frac{\partial G}{\partial T}\right)_{N,p}=-S \qquad \left(\frac{\partial G}{\partial p}\right)_{T,N}=V \tag{15}$$

Now to relate G and μ, we note that G increases linearly with N, which is the number of molecules in the system. T and p do not change when two identical systems are put together but G doubles when two identical systems are put together because G is proportional to N. So

$$G = N\,F(T,p) \tag{16}$$

where F is a function of T and p and not N. So

$$\left(\frac{\partial G}{\partial N}\right)_{T,p} = F(T,p) \tag{17}$$

Therefore, $F = \mu$ (from (15)) and G is related to the chemical potential, μ, via

$$G = N\,\mu(p,T) \tag{18}$$

where N is the number of molecules in the system.

The two terms in the numerator of (9) are found using the thermodynamic relation,

$$\left(\frac{\partial G}{\partial T}\right)_{N,p} = -S \tag{19}$$

where S is the entropy of the system. Since N, the number of molecules in the system does not depend on temperature, we can write as follows

$$\left(\frac{\partial \mu}{\partial T}\right)_{p} = \left(\frac{\partial\left(\frac{G}{N}\right)}{\partial T}\right)_{p} = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_{N,p} = -\frac{S}{N} = -s \tag{20}$$

where s is the entropy per molecule.

The two terms in the denominator of (9) are found using the thermodynamic relation,

$$\left(\frac{\partial G}{\partial p}\right)_{N,T} = V \tag{21}$$

where V is the volume occupied by the N molecules. Again, because the number of molecules in the system does not depend on pressure, we can write

$$\left(\frac{\partial \mu}{\partial p}\right)_{T} = \left(\frac{\partial \frac{G}{N}}{\partial p}\right)_{T} = \frac{1}{N}\left(\frac{\partial G}{\partial p}\right)_{N,T} = \frac{V}{N} = v \tag{22}$$

where v is the volume per molecule.

Combining (20) and (22) with (9), we get

$$\frac{dp}{dT} = \frac{\left[\left(\frac{\partial \mu_l}{\partial T}\right)_p - \left(\frac{\partial \mu_g}{\partial T}\right)_p\right]}{\left[\left(\frac{\partial \mu_g}{\partial p}\right)_T - \left(\frac{\partial \mu_l}{\partial p}\right)_T\right]} = \frac{\left[s_g - s_l\right]}{\left[v_g - v_l\right]} \tag{23}$$

Note that $s_g - s_l$ is the increase in entropy of the system when we transfer one molecule from the liquid to the gas phase. v_g-v_l is the increase in the volume of the system when we transfer one molecule from the liquid to the gas phase.

We know that the internal heat conversion in moving a molecule from the liquid state to the vapor state is L_m which is the latent heat per molecule. The change in entropy is the change in energy divided by temperature such that

$$\left(s_g - s_l\right) = \frac{\Delta Q}{T} = \frac{L}{T} \tag{24}$$

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We combine these to get the change in the equilibrium vapor pressure with temperature as

$$\frac{dp}{dT} = \frac{L}{T\Delta v} \tag{25}$$

The next step is to recognize that the volume taken up by the molecule in the gas phase is much larger than the volume taken up by the molecule in the liquid phase.

$$\Delta v \cong v_g = \frac{V_g}{N_g} \tag{26}$$

We can then use the microscopic form of the ideal gas law, $P\ V = N\ k_B\ T$ to get

$$v_g = \frac{V}{N} = \frac{k_B T}{p} \tag{27}$$

which we substitute in to get

$$\frac{dp}{dT} = \frac{L_m}{T\Delta v} \cong \frac{L_m}{T v_g} = \frac{pL_m}{k_B T^2} \tag{28}$$

Converting this to the macroscopic version

$$\frac{dp}{dT} = \frac{p}{T^2}\frac{L_m N_A}{k_B N_A} = \frac{pL_{mole}}{R^* T^2} = \frac{p}{T^2}\frac{L_{mole}}{\mu}\frac{\mu}{R^*} = \frac{pL_v}{R_v T^2} \tag{29}$$

$$\frac{dp}{dT} = \frac{pL_v}{R_v T^2} \tag{30}$$

where L_v is the latent heat of vaporization in J/kg and R_v is the gas constant for water in J/kg/K. This is the form of the Clausius Clapeyron we usually see and use with e_s equal to the saturation vapor pressure of water.

$$\frac{de_s}{dT} = \frac{e_s L_v}{R_v T^2} \tag{31}$$

As noted previously, the temperature dependence of L_v means that precise integration of (31) produces more complicated forms of the Clausius Clapeyron equations than one might expect.

there are a lot of different formulations that account for the temperature dependence. See http://cires.colorado.edu/~voemel/vp.html for a summary of these.

A plot of the Clausius Clapeyron equations for water vapor is shown below.