

## The Clausius-Clapeyron and the Kelvin Equations

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### Abstract

This lecture deals with the phase changes. In particular, starting from heuristic considerations, a quantity called Gibbs free energy is defined. This quantity is conserved during isothermal and isobaric transformations and is used to determine how the equilibrium pressure between two different phases changes with temperature. This law is called the Clausius-Clapeyron equation and is one of the fundamental laws of cloud microphysics. The Clausius-Clapeyron equation for the three different phase changes is represented in the  $P$ - $T$  diagram. The properties of these relationships are briefly described as well as some examples of their applications. Some preliminary considerations are done concerning the role of Clausius-Clapeyron equation on the precipitation formation. The Clausius-Clapeyron equation does not describe the most general possible relationship between the equilibrium pressure and temperature because it does not take into account the geometry of the system. A generalized form of the Gibbs free energy that takes into account even the energy needed to create a surface is developed. With this generalized form the dependency of equilibrium pressure in a spherical geometry is developed. This relationship is called Kelvin's law. The role of Kelvin's law in the occurrence of supersaturation, then in the formation of cloud droplets is discussed.

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### The Gibbs free energy

Water vapour can be considered as a perfect gas (i.e., described by the ideal gas law  $e = \rho RT$  where  $e$  is its partial pressure,  $R$  its constant and  $\rho$  its density) almost for all the real situations apart when condensation occurs. When condensation takes place, e.g., during an isothermal compression, what is observed is that even the vapour pressure remains constant up to the moment in which all the vapour is condensed. This fact cannot be explained nor by the ideal gas law, neither by the Van der Waals equation of state, moreover the pressure value at which condensation begins is, for pure water, function of temperature only. This value is called “saturation vapour pressure” and it should be extremely interesting to know in advance its value for a given temperature to realize how far we are, in terms of amount of vapour pressure from saturation. To know how saturation vapour pressure changes as a function of temperature we cannot, obviously, use nor the ideal gas law, neither the van der Waals but we have to base our thoughts on more fundamental laws, in particular on the first law of thermodynamic.

$$\frac{dQ}{dt} = \frac{dU}{dt} + e \frac{dV}{dt}$$

We apply the first law to the idealized transformation above mentioned, that is the isothermal compression at saturation on a system composed by liquid water and water vapour.

If we integrate the first law between the times  $t_1$  and  $t_2$  we obtain

$$\int_{t_1}^{t_2} \frac{dQ}{dt} dt = \int_{t_1}^{t_2} \frac{dU}{dt} dt + \int_{t_1}^{t_2} e \frac{dV}{dt} dt .$$

Because in the above transformation (constant temperature) during the condensation  $e$  remains constant, defining as  $l$  the amount of heat released (absorbed) when a unitary mass of vapour is condensed (evaporated), we can write

$$l \Delta M = U(t_2) - U(t_1) + e(V(t_2) - V(t_1))$$

dividing by the total amount of water vapour  $\Delta M$  condensed and introducing the specific variables for internal energy and volume (i.e.,  $u$  and  $\alpha$ ) we have

$$l = u(t_2) - u(t_1) + e(\alpha(t_2) - \alpha(t_1)) .$$

At this point it is useful to introduce the specific entropy  $s$  for unit mass defined as

$$\frac{ds}{dt} = \frac{1}{T} \frac{dq}{dt}$$

Because in the above transformation temperature  $T$  is kept constant, integrating the specific temperature between the same times  $t_1$  and  $t_2$  we obtain

$$\int_{t_1}^{t_2} \frac{ds}{dt} dt = \int_{t_1}^{t_2} \frac{1}{T} \frac{dq}{dt} dt$$

that is

$$s(t_2) - s(t_1) = \int_{t_1}^{t_2} \frac{1}{T} \frac{dq}{dt} dt = \frac{1}{T} l$$

or equivalently

$$T(s(t_2) - s(t_1)) = \int_{t_1}^{t_2} \frac{dq}{dt} dt = l$$

Equating the two specific latent heats we obtain the relationship

$$T(s(t_2) - s(t_1)) = u(t_2) - u(t_1) + e(\alpha(t_2) - \alpha(t_1))$$

that rearranged becomes

$$u(t_1) + e\alpha(t_1) - T s(t_1) = u(t_2) + e\alpha(t_2) - T s(t_2)$$

which states that we can define a quantity (usually denoted by the  $g$  letter) which is constant during the phase transitions (in isobaric and isothermal transformations). This quantity is called *Gibbs free energy* (i.e.,  $g = u + p\alpha - Ts$ ) and it is essentially the specific enthalpy (i.e.,  $h = u + p\alpha$ ) diminished by the product of temperature for specific entropy (i.e.,  $Ts$ ).

Thanks to its constance during phase transitions, specific Gibbs internal energy can be used to describe how the saturation vapour pressure changes with temperature, in fact the specific Gibbs free energy is constant for the two phases (vapour and liquid), then we can write

$$\frac{dg_l}{dT} = \frac{dg_v}{dT}$$

equation that, using the definition of Gibbs free energy, becomes

$$\frac{d}{dT}(u + e\alpha - Ts)_l = \frac{d}{dT}(u + e\alpha - Ts)_v$$

expanding the derivatives we obtain

$$\frac{du_l}{dT} + \frac{de_l}{dT}\alpha_l + e_l \frac{d\alpha_l}{dT} - s_l - T \frac{ds_l}{dT} = \frac{du_v}{dT} + \frac{de_v}{dT}\alpha_v + e_v \frac{d\alpha_v}{dT} - s_v - T \frac{ds_v}{dT}$$

or equivalently

$$\left(\frac{du_l}{dT} + e_l \frac{d\alpha_l}{dT}\right) + \frac{de_l}{dT}\alpha_l - s_l - T \frac{ds_l}{dT} = \left(\frac{du_v}{dT} + e_v \frac{d\alpha_v}{dT}\right) + \frac{de_v}{dT}\alpha_v - s_v - T \frac{ds_v}{dT}$$

then applying the following form of the first law of thermodynamics

$$\frac{dq}{dT} \frac{dT}{dt} = \left(\frac{du}{dT} + e \frac{dv}{dT}\right) \frac{dT}{dt}$$

and the following definition of entropy

$$\frac{ds}{dT} \frac{dT}{dt} = \frac{1}{T} \frac{dq}{dT} \frac{dT}{dt}$$

both based on the fact that the only quantity we varies is temperature, the above equation becomes

$$\left(\frac{dq_l}{dT}\right) + \frac{de_l}{dT}\alpha_l - s_l - \frac{dq_l}{dT} = \left(\frac{dq_v}{dT}\right) + \frac{de_v}{dT}\alpha_v - s_v - \frac{dq_v}{dT}$$

then

$$\frac{de_l}{dT}\alpha_l - s_l = \frac{de_v}{dT}\alpha_v - s_v .$$

Since the vapour and liquid pressure are the same, i.e., the saturation vapour pressure  $e_v = e_l \equiv e_s$ , we obtain

$$\frac{de_s}{dT} = \frac{s_v - s_l}{\alpha_v - \alpha_l}$$

This equation solves formally our problem, because it gives a defined form for the variation of saturation vapour pressure with temperature, moreover it gives us useful hints for the physical interpretation of the saturation vapour pressure derivative. In fact we can say that the rate of change of saturation vapour pressure with temperature is the entropy rate of change for the given change in specific volume in the transition between the two phases. In other words we can say that saturation vapour pressure changes (increases) with temperature because specific entropy increases with temperature more in vapour than in liquid phase. Apart from its interesting physical interpretation the above equation is still in a poorly useful form. A better form can be easily obtained remembering the result we obtained to define the Gibbs internal energy, i.e., the difference in the specific entropies of liquid and solid water during the phase transition is the specific latent heat of

vaporization (condensation) divided by the temperature at which the transition takes place. With this in mind we obtain

$$\frac{de_s}{dT} = \frac{1}{T} \frac{l}{\alpha_v - \alpha_l}$$

which is the usually adopted functional dependence of saturation vapour pressure from absolute temperature, universally known as Clausius-Clapeyron equation. This equation *mutatis mutandis* can be used to describe all the change of phase from vapour to liquid, from vapour to solid and from liquid to solid. In the latter cases latent heats of sublimation and solidification (i.e., sublimation minus condensation) have to be used instead of latent heat of condensation. This equation can be integrated in principle but practically this can be done only assuming a functional dependency from temperature of latent heats and specific volumes. Some considerations, however, can be done even without the integration. In particular usually, being latent heats positive defined, the saturation pressure increases or decreases with temperature according to the interplay between the specific volumes of the two phases. In other words, usually saturation pressure for vapour and liquid phases increases with temperature because vapour density is lower than liquid density. The same happens for many liquid and solid phases, apart from water because its density is lower for ice than for liquid

As told before, the water Clausius-Clapeyron equation for the usual atmospheric conditions can be quite easily integrated with a few simple assumptions. The simplest possible situation is that of vapour and liquid phases. We start assuming that latent heat of condensation is constant with temperature and that liquid water specific volume (inverse of density) can be neglected when compared with vapour specific volume. Water latent heat of condensation changes by about 6% from its  $l=2501 \text{ J/g}$  at  $0^\circ\text{C}$ . We can go a step further just using one more assumption, that is the ideal gas law for the water vapour to describe the functional dependence of  $\alpha_v$  from temperature, i.e.,  $e\alpha_v = RT$ . With these assumptions the Clausius-Clapeyron equation becomes

$$\frac{de_s}{dT} \simeq \frac{1}{T} \frac{l}{\alpha_v} \simeq \frac{1}{T} \frac{l e_s}{RT} = \frac{l e_s}{RT^2}$$

which can be easily integrated giving an exponential dependence of  $e_s$  from temperature. A greater accuracy (i.e., ability of reproducing reality) can be obtained introducing into the above equation the dependence of latent heat from temperature. This can be easily done using the first law of thermodynamics and in particular a result we obtained in defining the Gibbs free energy to determine the latent heat of condensation, that is

$$l = u(t_2) - u(t_1) + e(\alpha(t_2) - \alpha(t_1))$$

where the index  $t_l$  is referring to the liquid phase while  $t_2$  to the vapour one (in this way  $l$  is positive). This equation can be simplified remembering that  $\alpha_2 \gg \alpha_1$  and confusing again water vapour with an ideal gas, then

$$l = u(t_2) - u(t_1) + e\alpha(t_1) = u(t_2) - u(t_1) + RT$$

Differentiating the above equation with respect to temperature, we obtain

$$\frac{dl}{dT} = \frac{d}{dT}(u(t_2)) - \frac{d}{dT}(u(t_1)) + \frac{d}{dT}(RT)$$

remembering that  $u(t_2)$  and  $u(t_1)$  are the internal energies of liquid water and water vapour, by

definition their derivatives represent the specific heats of water vapour at constant volume  $c_{vv}$  (remember that we still consider vapour as an ideal gas) and the specific heat of water  $c_w$ . Then we obtain

$$\frac{dl}{dT} = c_{vv} - c_w + R$$

or, remembering that  $R = c_{pv} - c_{vv}$

$$\frac{dl}{dT} = c_{pv} - c_w$$

which states us that if you do not want to consider constant with temperature the latent heat of condensation, you can at least consider constant with temperature its derivative. Then, fixing a reference status  $(l_0, T_0)$ , we can obtain the functional dependence of latent heat from temperature

$$l = (c_{pv} - c_w)(T - T_0) + l_0$$

that can be used into the Clausius-Clapeyron equation to obtain a preciser dependency of saturation vapour pressure from temperature. Apart from this specific use, the above equation tells us that

$$\Delta l = c_{pv} \Delta T - c_w \Delta T = \Delta Q_{pv} - \Delta Q_w$$

which means that when temperature changes the variations in latent heat of condensation is equal to the difference in the amount of heat absorbed (released) by two unitary masses of vapour and liquid water at constant pressure. This is not surprising, since that difference in heats has to be released (absorbed) when water vapour is made to condense (evaporate) keeping constant temperature (remember that condensation is a constant pressure process).

Before to conclude the discussion on the Clausius-Clapeyron equation it is just worth to spend a few more words on the liquid and solid transitions of phase. For them the equation assumes the form

$$\frac{de_s}{dT} = \frac{1}{T} \frac{l}{\alpha_l - \alpha_i}$$

where  $l$  in this case is the latent heat of solidification and  $e_s$  in this case is the pressure exerted by liquid over solid phase when they are in equilibrium (i.e., nor increasing of liquid part neither solid one for a closed system). It is interesting to apply this equation to water because, since  $T$  and  $l$  are positive defined, the sign of the derivative (i.e., the slope of  $e_s$  in the  $PT$  diagram) is that of  $(\alpha_l - \alpha_i)$ . For water this is negative since ice density is lower than liquid one. With this in mind we can produce the  $PT$  diagram for the three phases (liquid, solid and vapour) of water.

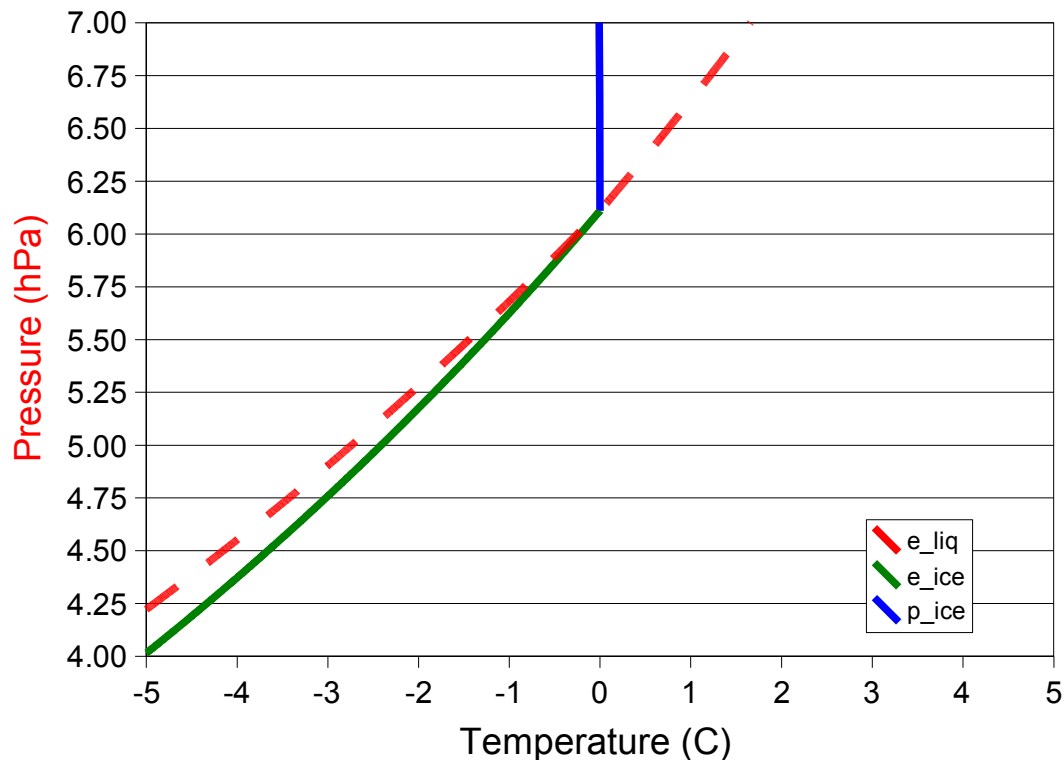


Figure. Water equilibrium pressures of liquid over solid (solid blue line), of vapour over liquid (dashed red line) and of vapour over solid (solid green).

From the above picture it is quite clear that equilibrium pressure over liquid is slightly higher over liquid than over ice. From the molecular point of view this means that water molecules escape easily from water than from ice, then reaching farther (i.e, for higher pressures) the equilibrium with the vapour.

Concerning the equilibrium pressure between liquid and solid, as described above, it decreases with increasing temperature. According to our naïve interpretation, we can imagine that for a fixed negative temperature you have to compress a lot ice to reduce its density -then reducing the intramolecular distances- making a little bit easy their escape from the ice phase in favour of the liquid one. The slope of equilibrium pressure between solid and liquid phase in the  $P$ - $T$  diagram is pretty steep (almost vertical) of the order of  $de_s/dT \sim -10^5 \text{ hPa K}^{-1}$ , inverting it we can see that freezing level decreases by nearly  $\Delta T \sim 0.01 \text{ K}$  when we increase pressure by one atmosphere ( $1013 \text{ hPa}$ ). This means that you can find liquid water even below the classical freezing level just increasing (a lot) pressure. However the sensitivity of melting point from pressure is so low that only in systems characterized by high pressures can take advantage from this mechanism. The classical example is represented by glaciers, whose base can host a thin liquid layer even for negative Celsius temperatures. Of course, dealing with glaciers composed by other substances, e.g.  $\text{CO}_2$ , as can happen in other planets, this effect might not take place when the solid phase of the specific substance has a higher density than the liquid one.

All the three equilibrium pressures for all the substances intersect on a point (called triple point) that for water coincides with the zero Celsius (i.e.,  $273.15 \text{ K}$ ). At the triple point all the three phases can coexist. The triple point is the key quantity when dealing with changes of phase, in fact as shown in the previous lectures, even if at standard atmospheric pressures both water and carbon dioxide are vapours, their behaviour is quite different. We have to take care of water vapour for the change of phase, while we can almost forget carbon dioxide. The reason why this happens is that the triple point for carbon dioxide ( $\sim 216.5 \text{ K}$ ,  $-56 \text{ }^\circ\text{C}$ ) is lower than for water. Is the distance from the triple

point that makes impossible the phase transition of the carbon dioxide, otherwise we should take care even of its latent heat of evaporation ( $lv \sim 574 \text{ J/kg}$ ) and of solidification ( $ls \sim 184 \text{ J/kg}$ ) to understand and forecast the atmospheric behaviour.

*Table. Saturation vapour pressure over liquid water, ice and the corresponding latent heats. Reproduced from the Smithsonian Meteorological Tables (List, 1951).*

T°C	e_s (Pa)	e_i (Pa)	L_v->l (J/kg)	L_v->s (J/kg)	L_l->s(J/kg)
-40	19.5	12.85	2603	2839	236
-35	31.54	22.36	-	-	-
-30	51.06	38.02	2575	2839	264
-25	80.9	63.3	-	-	-
-20	125.63	103.28	2549	2838	289
-15	191.44	165.32	-	-	-
-10	286.57	259.92	2525	2837	312
-5	421.84	401.78	-	-	-
0	611.21	611.15	2501	2834	333
5	872.47		2489		
10	1227.94		2477		
15	1705.32		2466		
20	2338.54		2453		
25	3168.74		2442		
30	4245.2		2430		
35	5626.45		2418		
40	7381.27		2406		

### The dependence of saturation vapour pressure from geometry

Obtaining the Clausius-Clapeyron equation and the dependence of equilibrium pressure from temperature we use the free energy of Gibbs. This free energy is conserved during the bulk transition between vapour and liquid as demonstrated above. However, in some circumstances (very often observed in nature), dealing with bulk phases is not enough, in fact geometry may play a major role. We can tackle the problem just with some heuristic considerations, in fact if we want to split a water droplet in two parts we have to spend energy. This expenditure of energy is needed to break the links between water molecules to produce two distinct parts. But we can consider this energy expenditure as due to the formation of a greater surface enveloping water. Even if this can seem counter-intuitive, it is particularly convenient under the analytical point of view.

Returning back to our initial problem, defining as  $g_v$  and  $g_w$  the Gibbs free energies for unit mass of water vapour and liquid water respectively, assuming that the energy required to produce a unit surface of liquid phase is  $\sigma$ , the conservation of total energy requires

$$\frac{d}{dt}(M_v g_v + M_w g_w + \sigma A) = 0$$

where  $A$  is the surface of liquid phase and  $M_w$  and  $M_v$  are respectively the masses of liquid and vapour phases.

Mass conservation during phase transition requires that

$$\frac{d}{dt}(M_v) = -\frac{d}{dt}(M_w)$$

then expanding the above derivative we obtain

$$(g_w - g_v) \frac{dM_w}{dt} + \sigma \frac{d}{dt} A = 0$$

Assuming a spherical geometry we can express the water mass as a function of water density  $\rho$  and of the droplet radius  $r$ . Moreover we can rewrite even the droplet surface obtaining

$$(g_w - g_v) \rho_w \frac{4}{3} \pi 3 r^2 \frac{dr}{dt} + \sigma 4\pi 2r \frac{dr}{dt} = 0$$

where we assumed constant both the surface energy for unit surface and the density. Simplifying we obtain

$$\left( g_w - g_v + \frac{2\sigma}{r\rho_w} \right) \frac{dr}{dt} = 0$$

Since energy has to be conserved independently from the radius variation with time, we can conclude that

$$g_v = g_w + \frac{2\sigma}{r\rho_w}$$

This equation means that not all the bulk Gibbs free energy of vapour transfers into the liquid phase (per unit mass): an amount of it is spent in producing the surface. If the droplet radius diverge (infinite curvature, e.g., a “plane” droplet), we return back to what we used at the beginning of this lecture. To obtain the equilibrium pressure dependence from the geometry (radius in this case), we will now use the above generalize version of the Gibbs free energy conservation. In particular we will differentiate with respect to the radius  $r$ .

$$\frac{dg_v}{dr} = \frac{dg_w}{dr} + \frac{d}{dr} \left( \frac{2\sigma}{r\rho_w} \right)$$

To expand this derivative we have to remember that Gibbs free energy depend only from pressure  $p$  and temperature  $T$  (which we consider not dependent from radius), then

$$\frac{\partial g_v}{\partial p} \frac{dp}{dr} = \frac{\partial g_w}{\partial p} \frac{dp}{dr} - \frac{2}{r^2} \frac{\sigma}{\rho_w}$$

from the functional dependency of specific Gibbs free energy we have

$$\frac{\partial g_v}{\partial p} = \frac{1}{\rho_v} \quad \text{and} \quad \frac{\partial g_w}{\partial p} = \frac{1}{\rho_w}$$

Then with simple algebra we obtain

$$\frac{dp}{dr} = -\frac{2\sigma}{r^2} \left( \frac{\rho_v}{\rho_w - \rho_v} \right)$$



Remembering that at ordinary atmospheric conditions water vapour can be considered an ideal gas, we can write vapour density as a function of pressure and temperature, that is

$$\rho_v = \frac{p}{R_v T}$$

With relatively simple algebra we obtain the following differential equation

$$\frac{(\rho_w R_v T - p)}{p} \frac{dp}{dr} = -\frac{2\sigma}{r^2}$$

which can be solved integrating it from a generic radius  $r$  up to an infinite radius, giving

$$\ln\left(\frac{p}{p_\infty}\right) = \frac{2\sigma}{r \rho_w R_v T} + \frac{\rho_v (p - p_\infty)}{\rho_w p}$$

Since water density is higher than vapour density we can delete the last term on the right member obtaining the so called *Kelvin law for the equilibrium pressure*:

$$p = p_\infty e^{\frac{2\sigma}{r \rho_w R_v T}}$$

The interpretation of  $p_\infty$  is quite straightforward, remembering that the infinite radius corresponds to a flat surface. In other words it is the bulk equilibrium pressure we obtained with the Clausius Clapeyron equation.

Using the values normally observed in atmospheric conditions for the above Kelvin's law ( $R_v = 461$  J/kg K ;  $\sigma = 0.0073$  N m and  $\rho_w = 10^3$  kg/m<sup>3</sup>) we obtain

$$p = p_\infty e^{\frac{0.001}{r}}$$

where  $r$  is measured in microns.

From the above law it is clear that differences in the saturation (equilibrium) vapour pressure over water is really a weak function of radius. Nevertheless this dependence is extremely important for the development of cloud droplets and then the formation of precipitations. In particular it is clear that the saturation vapour pressure required to admit the formation of droplets of the order of a few hundredths of micron is extremely high, more than twice the maximum observed in nature. This means that condensation of water vapour is extremely difficult. Very small droplets can form easily under the statistical point of view, but they are stable only for very high pressures. On the contrary the pressure required for the equilibrium of large droplets (a few microns) is not so high, but they are statistically disadvantaged. This is the reason why condensation of pure water vapour (*homogeneous condensation* or *nucleation*) is quite rare in nature and the formation of clouds has to take place for different reasons, in particular we need what is called *heterogeneous condensation* which requires the presence of condensation nuclei. The same is true for the solid phase formation.

Figure. The ratio between equilibrium pressure for water over a spherical and flat surface as a function of the sphere radius.

