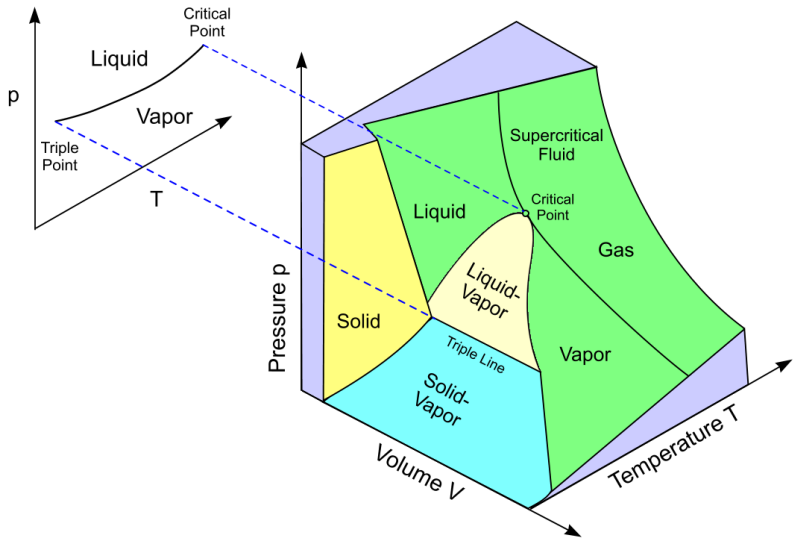
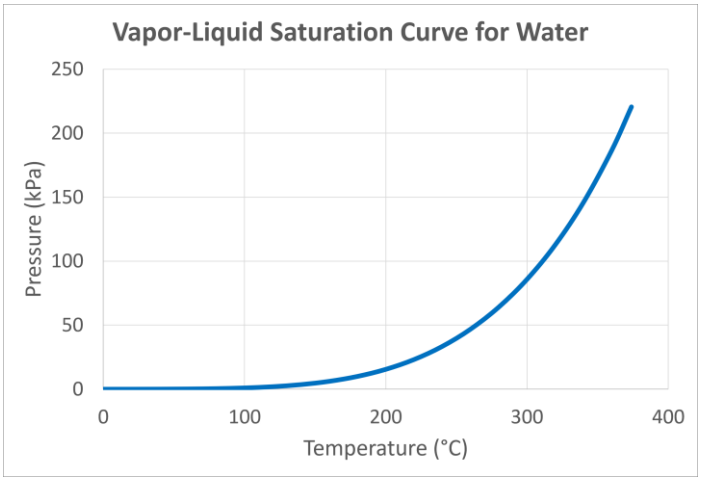
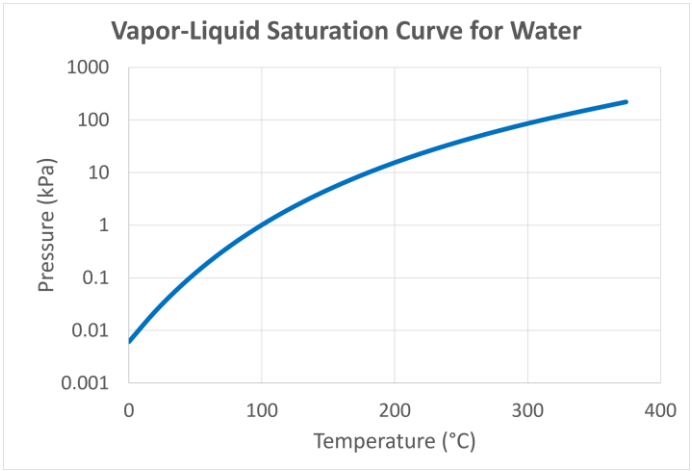
Lapse Rate. Prof. Ruiz (Doc), UNC-Asheville (1978-2021), DoctorPhys on YouTube.
Prerequisites: Chemistry, Physics I, II. Calculus I, II, III. Thermodynamics.

Chapter N. The Clausius-Clapeyron Equation. In our last section we showed that $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}$, which is called the Clapeyron equation. This derivative gives the linear version of the slope of the projected saturated liquid-vapor curve in the pressure-temperature plane rather than the log pressure scale of the p-V-T surface. Below we graph $p = p(T)$ purely from the actual data. The lower plot has log spacing for the pressure, making the plot convex.



Temperature (°C)	Saturated Vapor Pressure (kPa)
0.01	0.61165
20	2.3393
40	7.3849
60	19.946
80	47.414
100	101.42
120	198.67
140	361.54
160	618.23
180	1002.8
200	1554.9
220	2319.6
240	3346.9
260	4692.3
280	6416.6
300	8587.9
320	11284
340	14601
360	18666
373.946	22064





Our main goal in this chapter is to derive the Clausius-Clapeyron equation and see how well the data, Clapeyron equation, and Clausius-Clapeyron equation all compare. But first, we have a notational adjustment to make.

When we apply this saturated-vapor concept to meteorology we reserve p for total pressure, which consists of the partial pressure of dry air p_d and the partial pressure of the water vapor e. The saturation pressure from the Clapeyron equation is then relabeled e_s, where e clearly refers to water vapor and the subscript "s" indicates vapor saturation: $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha} \Rightarrow \frac{de_s}{dT} = \frac{l_v}{T\Delta\alpha}$.

$$\boxed{\frac{de_s}{dT} = \frac{l_v}{T\Delta\alpha}}$$ (Clapeyron Equation with Meteorology Notation)

We proceed to introduce two approximations that will transform the above Clapeyron equation into the Clausius-Clapeyron equation.

Approximation 1. The Change in Specific Volume. The change in specific volume $\Delta\alpha$ is the specific volume of the vapor formed minus the initial specific volume of the original liquid water. Since vapor takes up much greater space than water,

$$\Delta\alpha = \alpha_v - \alpha_l \approx \alpha_v .$$

The Clapeyron equation is transformed as follows by this first approximation.

$$\frac{de_s}{dT} = \frac{l_v}{T\Delta\alpha} \quad \Rightarrow \quad \frac{de_s}{dT} = \frac{l_v}{T(\alpha_v - \alpha_l)} \quad \Rightarrow \quad \frac{de_s}{dT} = \frac{l_v}{T\alpha_v}$$

Approximation 2. Ideal Gas. We describe the vapor as an ideal gas. We have encountered the ideal gas law for vapor: $e = \rho_v R_v T$ (9). Since $\rho_v = \frac{1}{\alpha_v}$, equivalent forms are $e = \frac{1}{\alpha_v} R_v T$ and $\frac{1}{\alpha_v} = \frac{e}{R_v T}$. To emphasize saturation we include the "s" subscript for the vapor pressure: $\frac{1}{\alpha_v} = \frac{e_s}{R_v T}$. We can substitute $\frac{e_s}{R_v T}$ for $\frac{1}{\alpha_v}$ in $\frac{de_s}{dT} = \frac{l_v}{T}\frac{1}{\alpha_v}$ and arrive at the following.

$$\frac{de_s}{dT} = \frac{l_v}{T}\frac{1}{\alpha_v} \quad \Rightarrow \quad \frac{de_s}{dT} = \frac{l_v}{T}\frac{e_s}{R_v T} \quad \Rightarrow \quad \frac{de_s}{dT} = \frac{e_s l_v}{R_v T^2}$$

(24) $$\boxed{\frac{de_s}{dT} = \frac{e_s l_v}{R_v T^2}}$$ (The Clausius-Clapeyron Equation)

Now we integrate the Clausius-Clapeyron equation. Technically $l_v = l_v(T)$, but the practice is to take l_v as being fairly constant over a given temperature range and integrate with it as a constant.

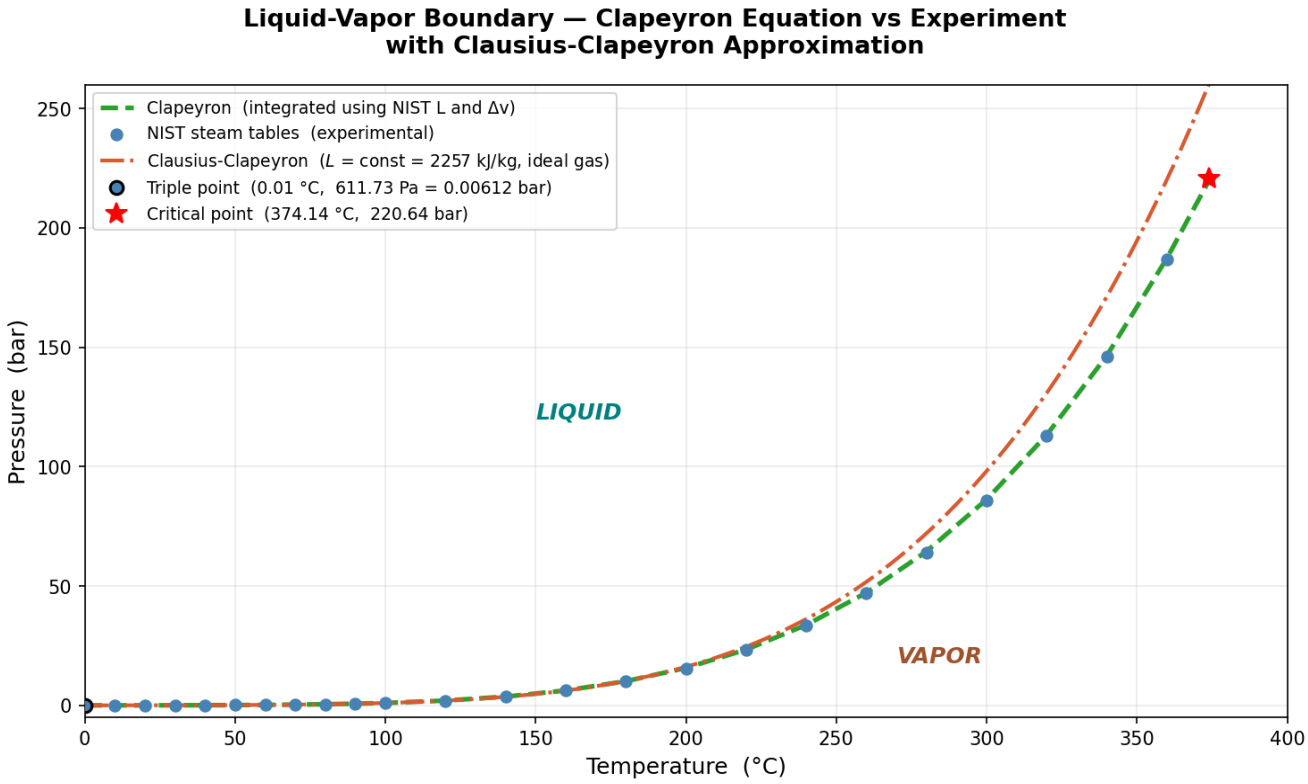
$$\frac{de_s}{dT} = \frac{e_s l_v}{R_v T^2} \quad \Rightarrow \quad \frac{1}{e_s}\frac{de_s}{dT} = \frac{l_v}{R_v T^2} \quad \Rightarrow \quad \int_{T_0}^{T} \frac{1}{e_s} de_s(T) = \int_{T_0}^{T} \frac{l_v}{R_v}\frac{1}{T^2} dT \quad \Rightarrow \quad \ln e_s(T)\Big|_{T_0}^{T} = \frac{l_v}{R_v}\int_{T_0}^{T} \frac{1}{T^2} dT$$

$$\Rightarrow \quad \ln e_s(T)\Big|_{T_0}^{T} = \frac{l_v}{R_v}\left(-\frac{1}{T}\right)\Bigg|_{T0}^{T} \quad \Rightarrow \quad \ln e_s(T) - \ln e_s(T_0) = -\frac{l_v}{R_v}\left(\frac{1}{T}\right)\Bigg|_{T0}^{T}$$

$$\ln\left[\frac{e_s(T)}{e_s(T_0)}\right] = -\frac{l_v}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right) \Rightarrow \frac{e_s(T)}{e_s(T_0)} = \exp\left[-\frac{l_v}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \Rightarrow e_s(T) = e_s(T_0)\exp\left[-\frac{l_v}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$$\boxed{e_s(T) = e_s(T_0)\exp\left[-\frac{l_v}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}$$

The above equation is the standard integrated form for the Clausius-Clapeyron equation. You can think of the Clausius-Clapeyron equation as an approximate Clapeyron equation. Remember that the typical integration of the Clausius-Clapeyron equation introduces another approximation, i.e., taking l_v to be constant over the range of temperature integration. In the graph below we compare the actual experimental data (blue dots), the integrated Clapeyron equation (green dashes), and the integrated Clausius-Clapeyron equation (red dot-dash curve).



The Clausius-Clapeyron equation starts to deviate from the data and Clapeyron equation at 240 °C. Here is why. Since one of the approximations in the Clausius-Clapeyron equation is taking l_v constant, we need to decide on which temperature should we pick l_v. For the above Clausius-Clapeyron plot the value $L = l_v$ was chosen for that the boiling point $T = 100°C$. From the table below we find that at temperature $T = 100°C$ the value for the enthalpy of vaporization is $L = l_v = 2256 \frac{\text{kJ}}{\text{kg}}$. Note that for the higher temperatures there is more and more drastic deviation from this value. Therefore, the Clausius-Clapeyron plot drifts more and more away from the data and more precise Clapeyron equation. Remember, the for the Clapeyron equation, we need to look data up in tables to figure out $p = p(T)$ from $\frac{dp}{dT} = \frac{l_v}{T\Delta\alpha}$. In that case, we pick l_v values depending on our temperatures T. We also accordingly pick $\Delta\alpha$ values from tables. However, at lower temperatures the Clausius-Clapeyron equation is excellent and we have a formula in closed form. We do not need to keep consulting tables for

$$e_s(T) = e_s(T_0)\exp\left[-\frac{l_v}{R_v}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$ once we choose $L = l_v = 2256 \frac{\text{kJ}}{\text{kg}}$ along with T_0 and $e_s(T_0)$.

We can pick $T_0 = 0.01°C$ with its corresponding $e_s(T_0) = 0.612$ kPa. The constant $R_v = 461.5 \frac{\text{J}}{\text{kg}\cdot\text{K}}$.

Temperature (°C)	Vapor Pressure (kPa)	Enthalpy of Vaporization $L = l_v$ (kJ/kg)
0.01	0.61165	2500.9
20	2.3393	2453.5
40	7.3849	2406.0
60	19.946	2354.7
80	47.414	2308.0
100	101.42	2256.4
120	198.67	2202.1
140	361.54	2144.3
160	618.23	2082.0
180	1002.8	2014.2
200	1554.9	1939.7
220	2319.6	1847.4
240	3346.9	1765.4
260	4692.3	1661.6
280	6416.6	1543.0
300	8587.9	1404.6
320	11284	1238.4
340	14601	1027.3
360	18666	719.8
373.946	22064	0.0

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