

VAPOUR PRESSURE EQUATION

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.35 - 5.36.

The Clausius-Clapeyron relation is a differential equation relating pressure and temperature on a phase boundary

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad (1)$$

where L is the latent heat for the phase transition and ΔV is the volume change. In order to solve this as a differential equation, we need to know L and ΔV as functions of P and T , which ordinarily we don't (or if we do, the relation is too complicated to solve analytically). However, if one of the phases is an ideal gas and we can take L constant over the region of interest, then usually the volume of the condensed phase (liquid or solid) is negligible compared to the gas phase. In this case, ΔV becomes essentially just V , the volume of the ideal gas, at temperature T and pressure P , that is, $\Delta V = V = nRT/P$ and if we consider 1 mole so that $n = 1$, we have

$$\frac{dP}{dT} = \frac{L}{TV} = \frac{LP}{RT^2} \quad (2)$$

We can then do the integration:

$$\frac{dP}{P} = \frac{L}{RT^2} dT \quad (3)$$

$$\ln P = -\frac{L}{RT} + \ln K \quad (4)$$

$$P = Ke^{-L/RT} \quad (5)$$

where K is a constant. This is known as the *vapour pressure equation*, and gives a measure of how the pressure at which the phase transition occurs varies as the temperature is raised.

As an example, we can consider the steam-water phase transition, for which data are given in Schroeder's Figure 5.11. Looking at the temperature range between 50° C and 100° C, we see that the latent heat isn't quite constant over this range, so we can use the average

$$L = \frac{1}{2}(42.92 + 40.66) \times 10^3 \text{ J mol}^{-1} \quad (6)$$

$$= 41.79 \times 10^3 \text{ J mol}^{-1} \quad (7)$$

The gas constant is

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad (8)$$

Using the given value of $P = 0.1234 \times 10^5 \text{ Pa}$ at $T = 50^\circ \text{ C} = 323 \text{ K}$ we find

$$K = 0.1234 \times 10^5 e^{41.79 \times 10^3 / 8.314 \times 323} = 7.07 \times 10^{10} \text{ Pa} \quad (9)$$

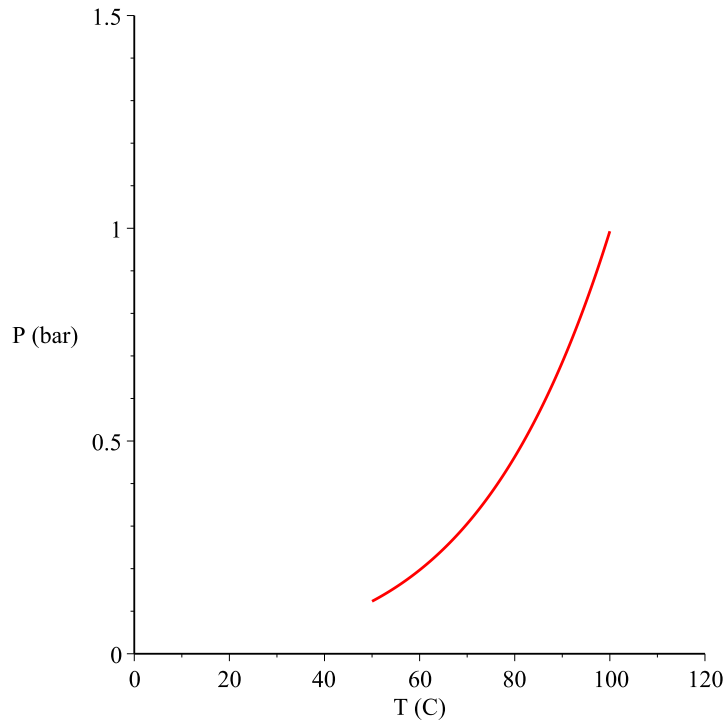
With this value of K , we can use 5 to predict the pressure at $T = 100^\circ \text{ C} = 373 \text{ K}$:

$$P(373) = 7.07 \times 10^{10} e^{-41.79 \times 10^3 / 8.314 \times 373} \quad (10)$$

$$= 9.93 \times 10^4 \text{ Pa} \quad (11)$$

The value given in Schroeder's Figure 5.11 is $P = 1.013 \text{ bar} = 10.13 \times 10^4 \text{ Pa}$ (that is, 1 atmosphere, since water boils at 100° C at sea level) so we're not too far off.

A plot of P versus V using 5 looks like this:



It has the same general shape as the steam-water phase boundary shown in Schroeder’s Figure 5.11.

We can invert 5 to find the boiling temperature for various altitudes. We get

$$T = \frac{L}{R \ln \frac{K}{P}} \tag{12}$$

Or, in centigrade:

$$T_c = \frac{L}{R \ln \frac{K}{P}} - 273 \tag{13}$$

Using the barometric equation, we found the atmospheric pressures at various altitudes. We can use this equation to add a column for the boiling point.

Altitude z (m)	$P(z)$ (atm)	T ($^{\circ}\text{C}$)
1430	0.844	95.9
3090	0.693	90.6
4420	0.592	86.5
8850	0.350	73.5

The last line is the height of Mt Everest.

We can get an estimate of the dependence of T on z , the height above sea level, as follows. We need to be careful to distinguish the boiling temperature T_w of the water from the surrounding air temperature T_a . From 2, the change ΔT_w as a result of a change ΔP in atmospheric pressure is

$$\Delta T_w = \frac{RT_w^2}{LP} \Delta P \quad (14)$$

From the barometric equation, the change in pressure due to an increase in height Δz is

$$\Delta P = -\frac{MgP}{RT_a} \Delta z \quad (15)$$

where M is the mass of a mole of air molecules. Inserting 15 into 14, we get

$$\Delta T_w = -\frac{Mg}{L} \frac{T_w^2}{T_a} \Delta z \quad (16)$$

In the limit, we get the differential equation

$$\frac{dT_w}{dz} = -\frac{Mg}{LT_a} T_w^2 \quad (17)$$

which we can integrate to get

$$\frac{1}{T_w} = \frac{Mg}{LT_a} z + A \quad (18)$$

$$T_w = \frac{1}{A + \frac{Mg}{LT_a} z} \quad (19)$$

for a constant of integration A . At $z = 0$, $T_w = 373$ so $A = 1/373 = 2.68 \times 10^{-3} \text{ K}^{-1}$. For a molar mass of $M = 0.029 \text{ kg}$ and an air temperature of $T_a = 10^\circ\text{C} = 283 \text{ K}$, we have

$$\frac{Mg}{LT_a} = \frac{(0.029)(9.8)}{(41.79 \times 10^3)(283)} = 2.4 \times 10^{-8} \text{ m}^{-1} \text{ K}^{-1} \quad (20)$$

$$\frac{Mg}{LT_a A} = \frac{2.4 \times 10^{-8}}{2.68 \times 10^{-3}} = 8.97 \times 10^{-6} \text{ m}^{-1} \quad (21)$$

Thus we can write 19 as

$$T_w = \frac{1}{A} \left(\frac{1}{1 + \frac{Mg}{LT_a A} z} \right) \quad (22)$$

$$= \frac{373}{1 + 8.97 \times 10^{-6} z} \quad (23)$$

where z is in metres. Even if z is several thousand metres, the z term in the denominator is quite small, so we can approximate it by

$$T_w \approx 373 \left(1 - 8.97 \times 10^{-6} z \right) \quad (24)$$

which shows that T_w is roughly linear in z . The slope is

$$\frac{dT_w}{dz} \approx -3.34 \times 10^{-3} \text{K m}^{-1} \quad (25)$$

which is a decrease in the boiling point of about 3.34 K per kilometre.

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