

## 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

$$(0.1) \quad \frac{dP}{dT} = \frac{L}{T\Delta V}$$

where  $L$  is the latent heat for the phase transition and  $\Delta V$  is the volume change. In order to solve this as a differential equation, we need to know  $L$  and  $\Delta V$  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,  $\Delta V$  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

$$(0.2) \quad \frac{dP}{dT} = \frac{L}{TV} = \frac{LP}{RT^2}$$

We can then do the integration:

$$(0.3) \quad \frac{dP}{P} = \frac{L}{RT^2} dT$$

$$(0.4) \quad \ln P = -\frac{L}{RT} + \ln K$$

$$(0.5) \quad P = Ke^{-L/RT}$$

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

$$(0.6) \quad L = \frac{1}{2} (42.92 + 40.66) \times 10^3 \text{ J mol}^{-1}$$

$$(0.7) \quad = 41.79 \times 10^3 \text{ J mol}^{-1}$$

The gas constant is

$$(0.8) \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

$$(0.9) \quad K = 0.1234 \times 10^5 e^{41.79 \times 10^3 / 8.314 \times 323} = 7.07 \times 10^{10} \text{ Pa}$$

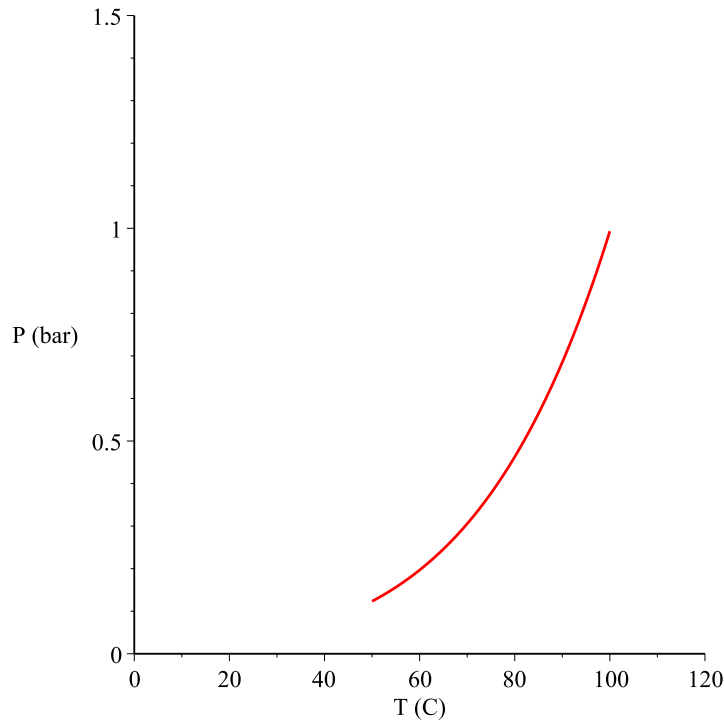
With this value of  $K$ , we can use 0.5 to predict the pressure at  $T = 100^\circ \text{ C} = 373 \text{ K}$ :

$$(0.10) \quad P(373) = 7.07 \times 10^{10} e^{-41.79 \times 10^3 / 8.314 \times 373}$$

$$(0.11) \quad = 9.93 \times 10^4 \text{ Pa}$$

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  $100^\circ \text{ C}$  at sea level) so we're not too far off.

A plot of  $P$  versus  $V$  using 0.5 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 0.5 to find the boiling temperature for various altitudes. We get

$$(0.12) \quad T = \frac{L}{R \ln \frac{K}{P}}$$

Or, in centigrade:

$$(0.13) \quad T_c = \frac{L}{R \ln \frac{K}{P}} - 273$$

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 0.2, the change  $\Delta T_w$  as a result of a change  $\Delta P$  in atmospheric pressure is

$$(0.14) \quad \Delta T_w = \frac{RT_w^2}{LP} \Delta P$$

From the barometric equation, the change in pressure due to an increase in height  $\Delta z$  is

$$(0.15) \quad \Delta P = -\frac{MgP}{RT_a} \Delta z$$

where  $M$  is the mass of a mole of air molecules. Inserting 0.15 into 0.14, we get

$$(0.16) \quad \Delta T_w = -\frac{Mg}{L} \frac{T_w^2}{T_a} \Delta z$$

In the limit, we get the differential equation

$$(0.17) \quad \frac{dT_w}{dz} = -\frac{Mg}{LT_a} T_w^2$$

which we can integrate to get

$$(0.18) \quad \frac{1}{T_w} = \frac{Mg}{LT_a} z + A$$

$$(0.19) \quad T_w = \frac{1}{A + \frac{Mg}{LT_a} z}$$

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

$$(0.20) \quad \frac{Mg}{LT_a} = \frac{(0.029)(9.8)}{(41.79 \times 10^3)(283)} = 2.4 \times 10^{-8} \text{ m}^{-1} \text{ K}^{-1}$$

$$(0.21) \quad \frac{Mg}{LT_a A} = \frac{2.4 \times 10^{-8}}{2.68 \times 10^{-3}} = 8.97 \times 10^{-6} \text{ m}^{-1}$$

Thus we can write 0.19 as

$$(0.22) \quad T_w = \frac{1}{A} \left( \frac{1}{1 + \frac{Mg}{LT_a A} z} \right)$$

$$(0.23) \quad = \frac{373}{1 + 8.97 \times 10^{-6} z}$$

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

$$(0.24) \quad T_w \approx 373 \left( 1 - 8.97 \times 10^{-6} z \right)$$

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

$$(0.25) \quad \frac{dT_w}{dz} \approx -3.34 \times 10^{-3} \text{K m}^{-1}$$

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

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