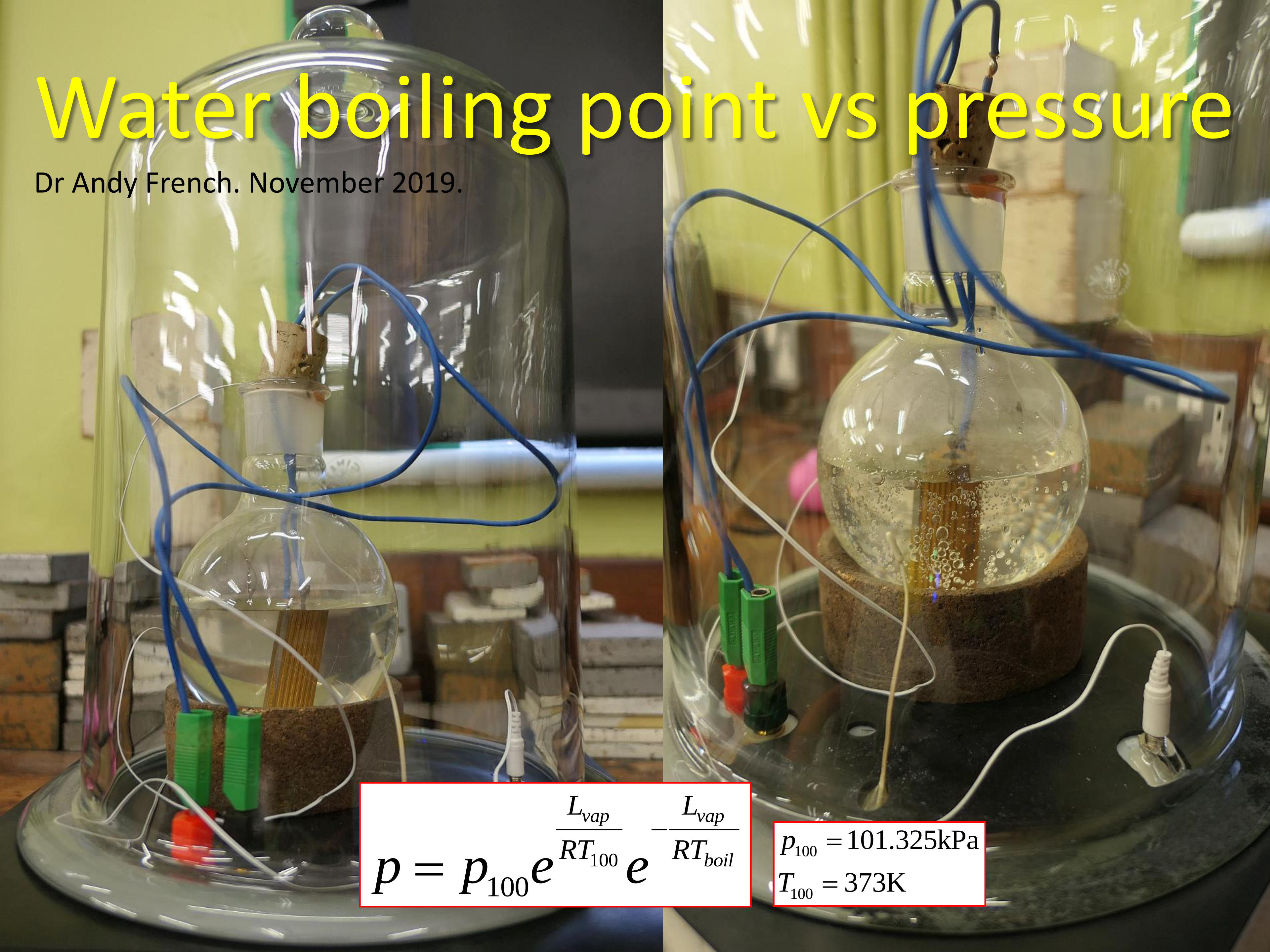
Water boiling point vs pressure

Dr Andy French. November 2019.

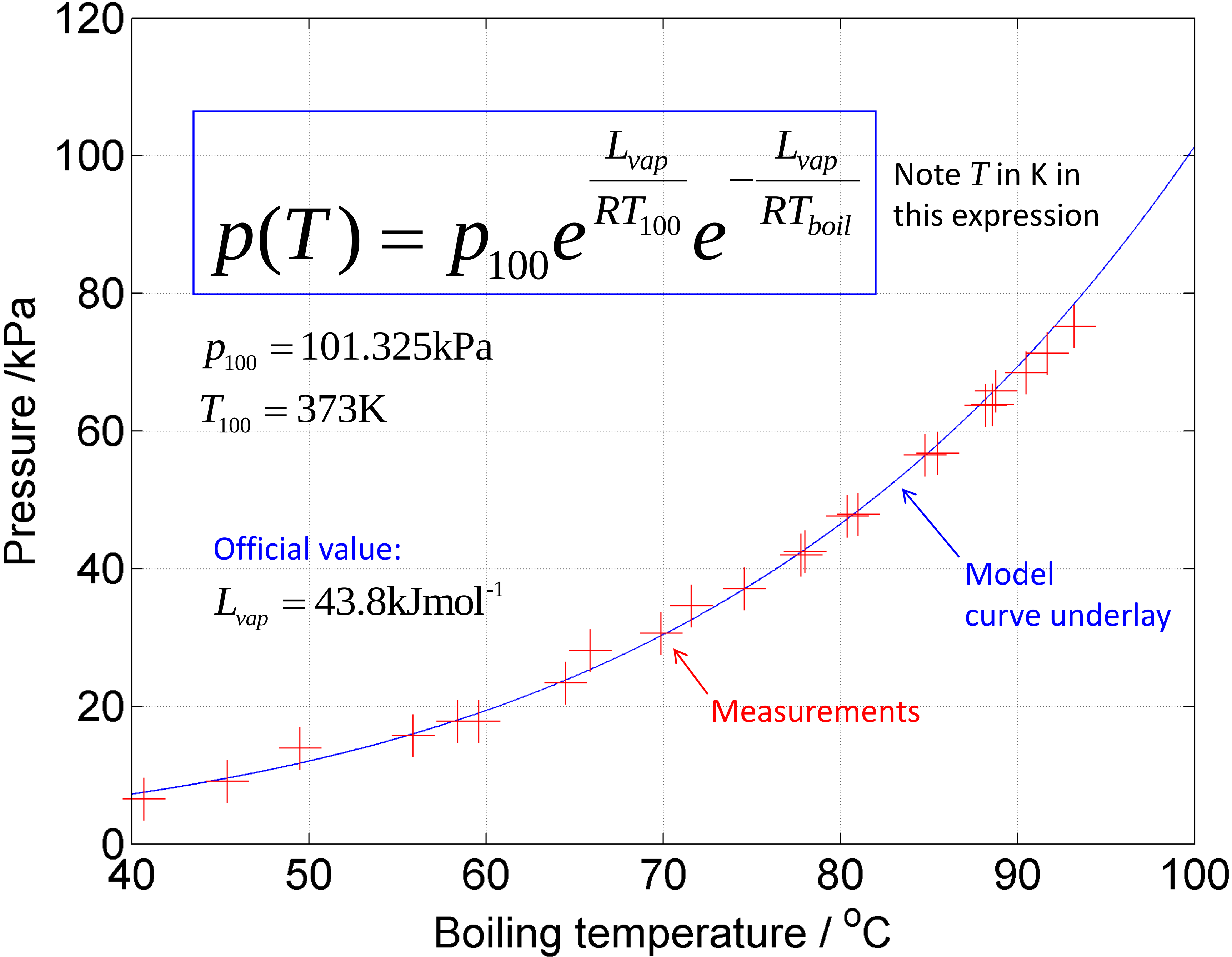


$$p = p_{100} e^{\frac{L_{vap}}{RT_{100}}} e^{-\frac{L_{vap}}{RT_{boil}}}$$

$$p_{100} = 101.325\text{kPa}$$

$$T_{100} = 373\text{K}$$

Pressure vs boiling temperature. L_{vap} = (42.7 +/-0.8) kJ/mol



$$p(T) = p_{100} e^{\frac{L_{vap}}{RT_{100}}} e^{-\frac{L_{vap}}{RT_{boil}}}$$

Note *T* in K in this expression

$$p_{100} = 101.325\text{kPa}$$

$$T_{100} = 373\text{K}$$

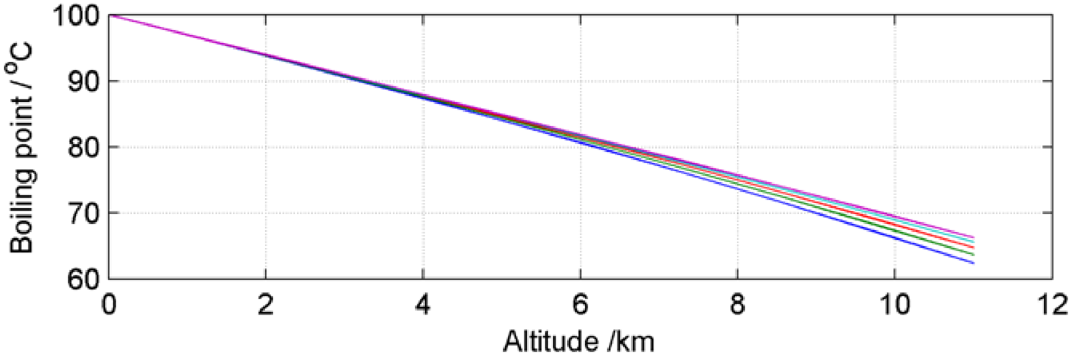
Official value:

$$L_{vap} = 43.8\text{kJmol}^{-1}$$

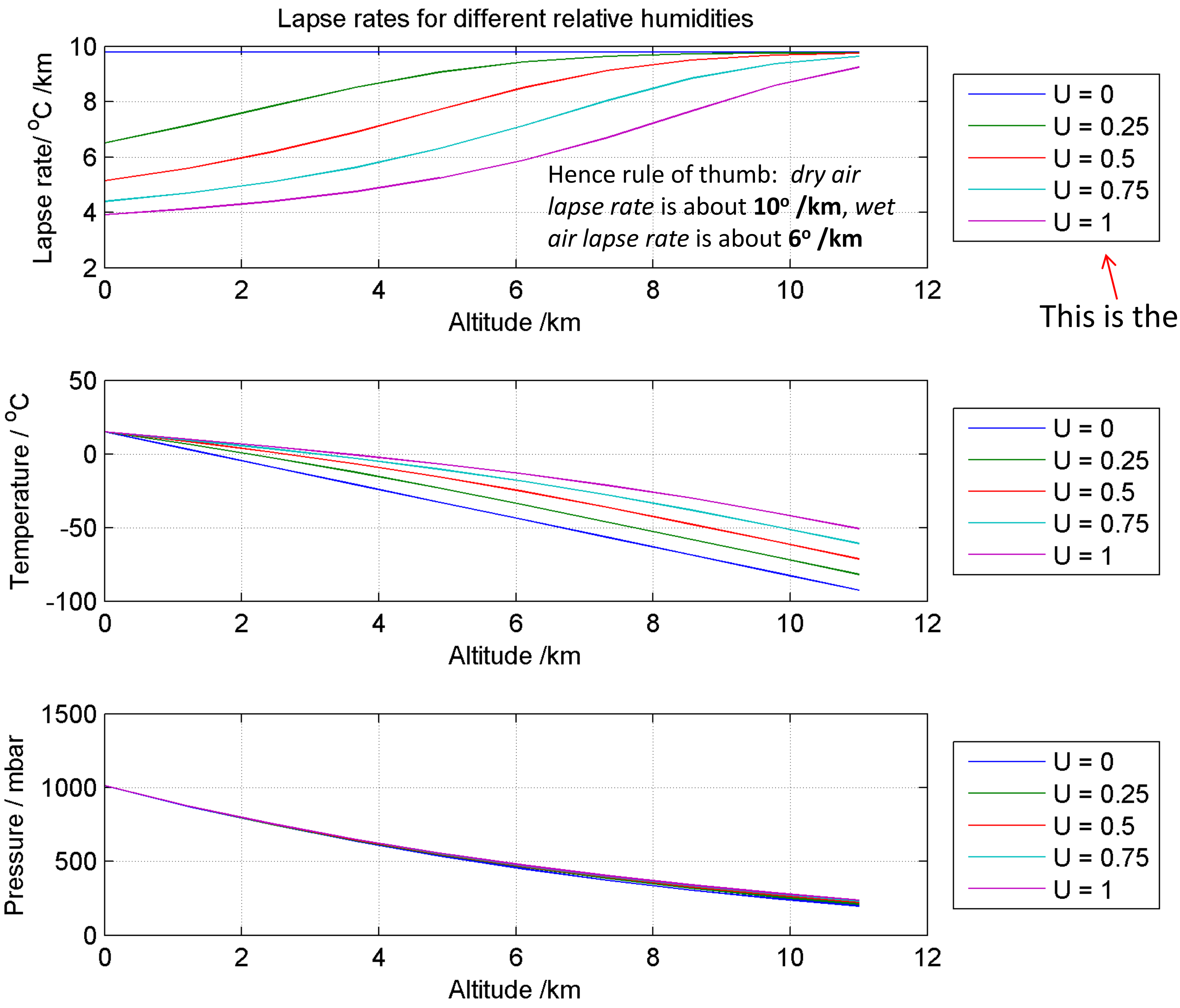
Model curve underlay

Measurements

Motivation: The boiling point of water *decreases* as atmospheric pressure *decreases*. You can observe this on a mountaineering expedition as you ascend in altitude.

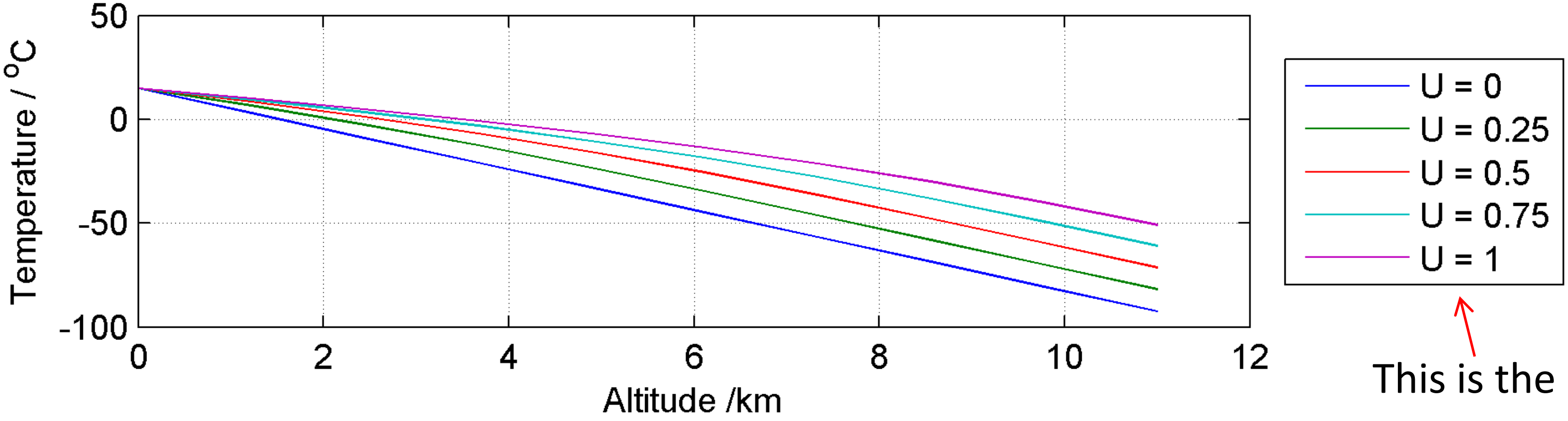


K2. August 2018

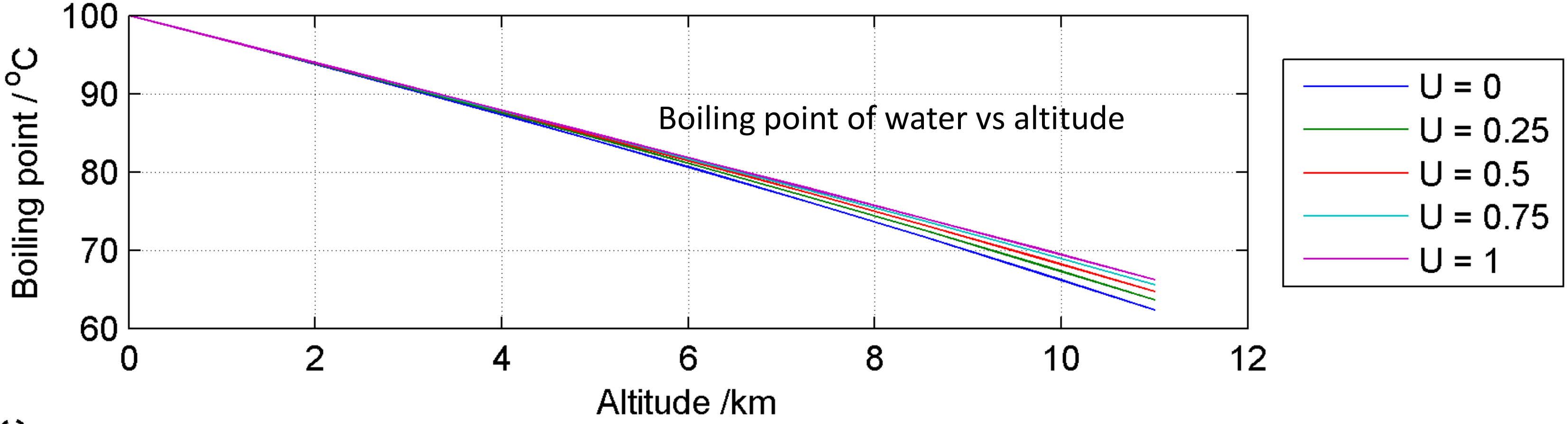


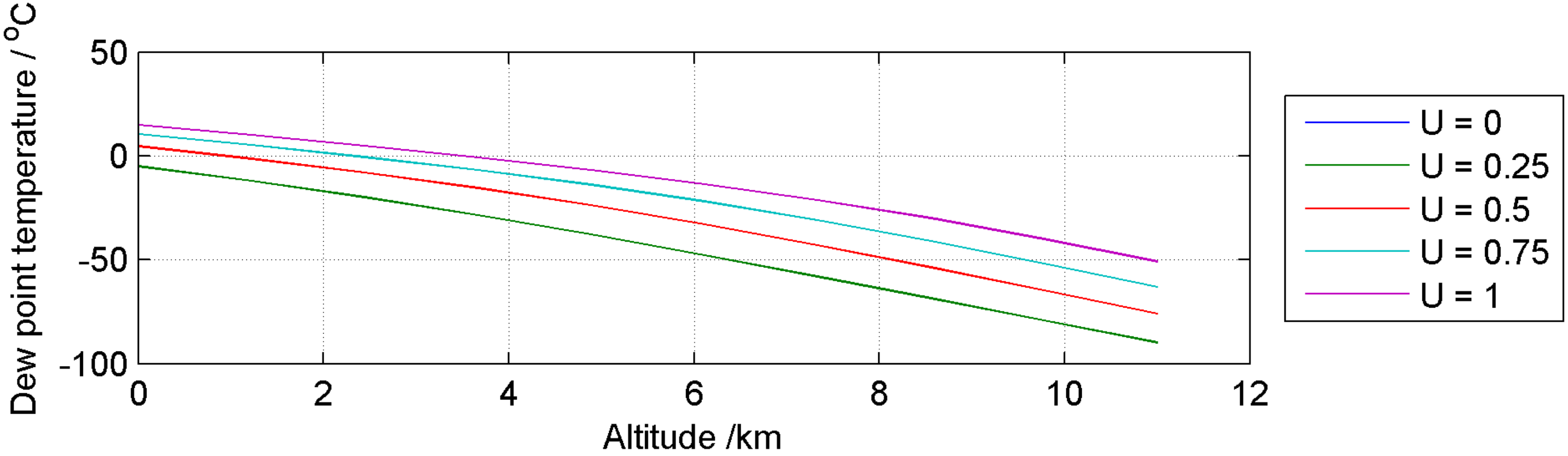
Hence rule of thumb: *dry air lapse rate* is about **10° /km**, *wet air lapse rate* is about **6° /km**

This is the humidity

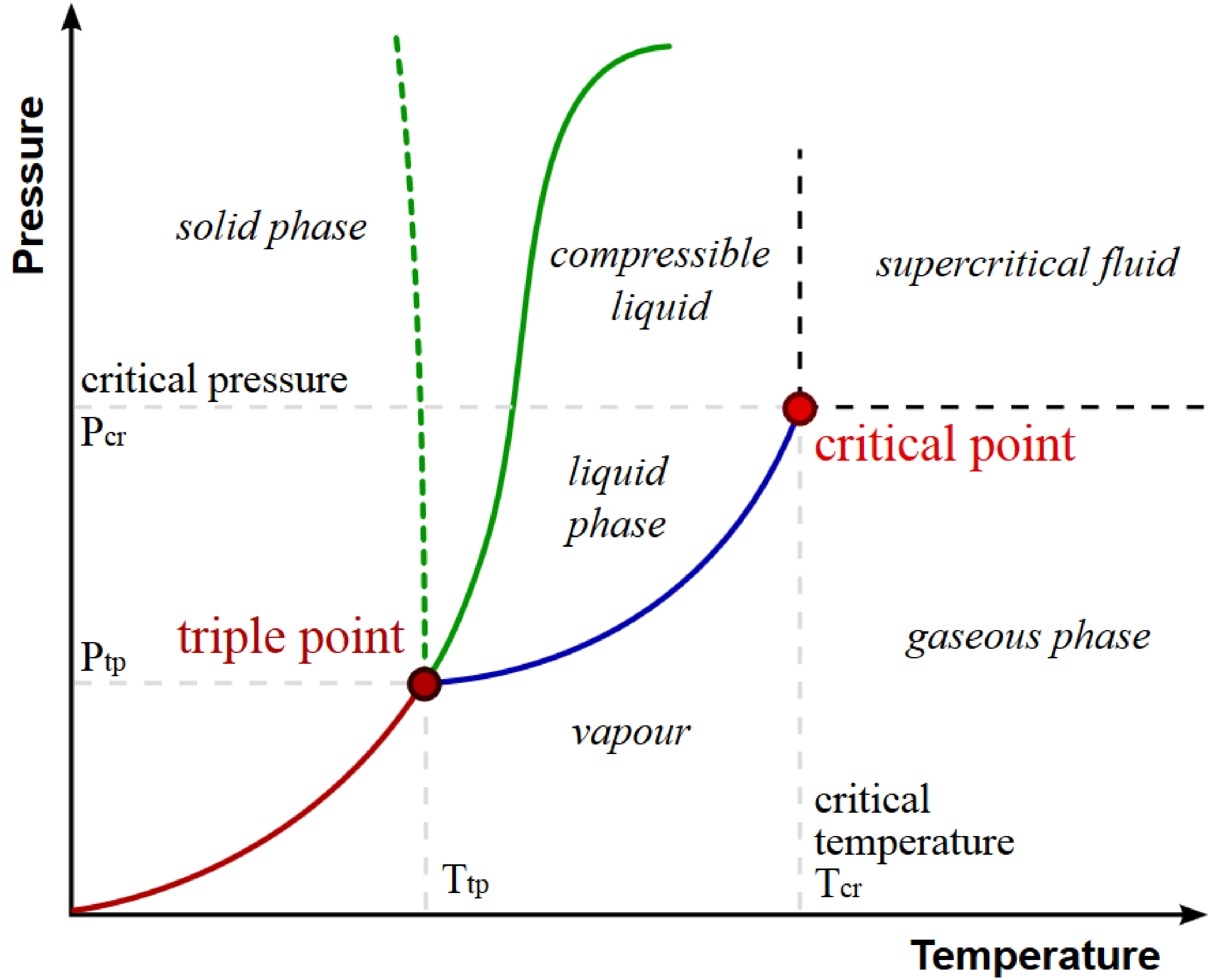


This is the humidity


Boiling point of water vs altitude



To **boil** water, it must undergo a *phase transition* from liquid to gas. This requires a certain amount of heat, *the latent heat of vaporization*, to break the inter-molecular bonds inherent in the water.



The gradient of a phase transition line in the p,T diagram is given by the *Clausius-Clapeyron equation:*

Pressure in Pascals (Pa)

Latent heat /Jmol^{-1}

$$\boxed{\frac{dp}{dT} = \frac{L_{vap}}{T\Delta V}}$$

Temperature in Kelvin

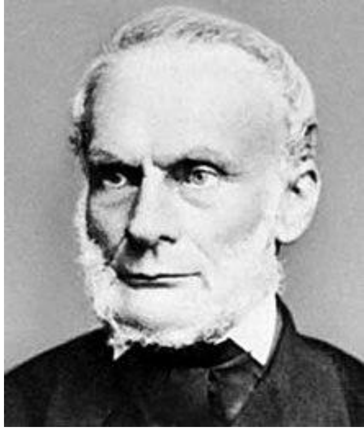
Volume change of 1 mole of substance during the phase transition

In a **liquid to gas** transition we can assume the volume change is sufficiently large as to ignore the original fluid volume. If one assumes the resulting gas is ***ideal***:

$$\Delta V = \frac{RT}{p}$$

Hence:

$$\boxed{\frac{dp}{dT} = \frac{L_{vap}}{RT^2}p}$$



Rudolph Clausius
1822-1888

Benoît
Clapeyron
1799-1864

We can use this relationship to determine the liquid-to-gas line in the p,T diagram if the latent heat of vaporization is assumed to be temperature independent. (In reality this is not the case, but is less of an issue at low temperatures – see next slide).

$$\frac{dp}{dT} = \frac{L_{vap}}{RT^2} p$$

$$\int_{P_*}^{P} \frac{1}{p} dp = \frac{L_{vap}}{R} \int_{T_*}^{T} \frac{1}{T^2} dT$$

$$\ln\left(\frac{p}{p_*}\right) = -\frac{L_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_*}\right)$$

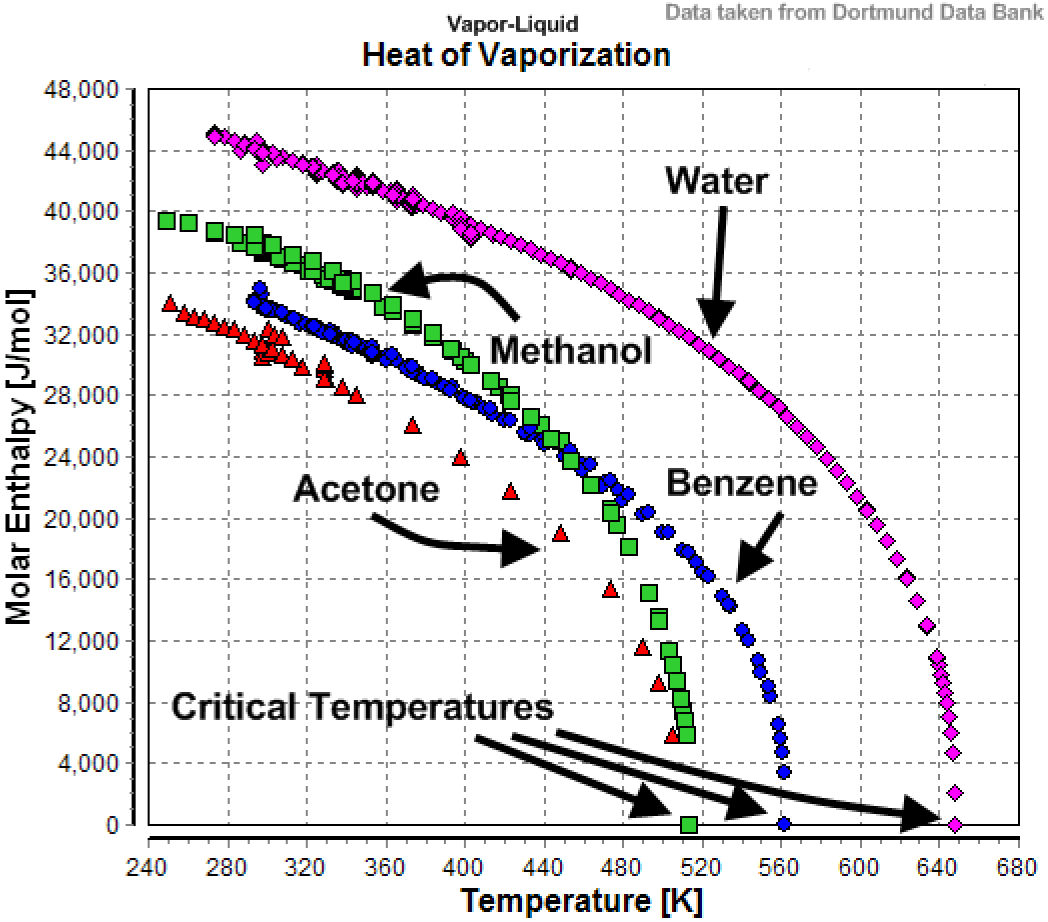
$$p = p_* e^{-\frac{L_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_*}\right)}$$

$$\boxed{T = \left(\frac{1}{T_*} - \frac{R}{L_{vap}} \ln\left(\frac{p}{p_*}\right)\right)^{-1}}$$

Since the temperature corresponds to the liquid-to-gas transition line, we can therefore derive an expression for the **boiling point** of a liquid relative to ambient temperature T and pressure p, as long as one fixed boiling point T_* and corresponding pressure p_* is known.

$$\boxed{T_{boil} = \left(\frac{1}{T_*} - \frac{R}{L_{vap}} \ln\left(\frac{p}{p_*} \right) \right)^{-1}}$$

Boiling point of water at different atmospheric pressures /mbar.



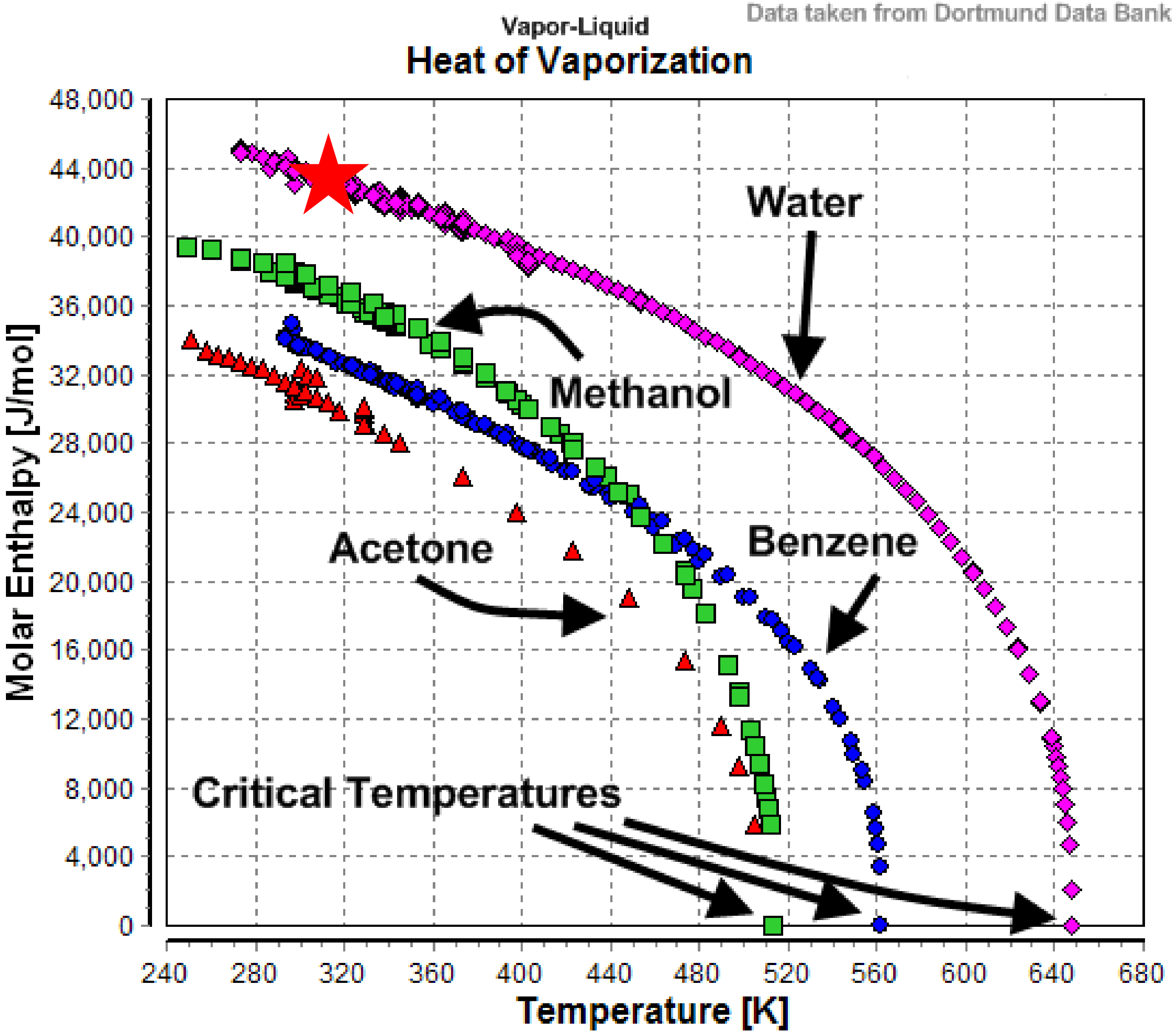
Latent heat of vaporization of water is

L_{vap} = 43.8 kJ mol^{-1} at 100°C and 1013.25 mbar ambient air pressure.

At ‘typical’ troposphere temperatures, a higher value of 45.07 kJ mol^{-1} is used in some calculations, such as the lapse rate model.

http://en.wikipedia.org/wiki/Lapse_rate
http://en.wikipedia.org/wiki/Enthalpy_of_vaporization
http://en.citizendium.org/wiki/Heat_of_vaporization

At around ambient temperatures of about 30 to 40 degrees C (i.e. 303K to 313K) molar latent heat of vaporization of water is about **43.8 kJ/mol/K**



$$T_{boil} = \left(\frac{1}{T_*} - \frac{R}{L_{vap}}\ln\left(\frac{p}{p_*}\right)\right)^{-1}$$

$$\frac{1}{T_{boil}} = \frac{1}{T_*} - \frac{R}{L_{vap}}\ln\left(\frac{p}{p_*}\right)$$

$$\frac{1}{T_{boil}} - \frac{1}{T_*} = \frac{R}{L_{vap}}\ln\left(\frac{p_*}{p}\right)$$

$$\therefore \ln\left(\frac{p_*}{p}\right) = \frac{L_{vap}}{R}\frac{1}{T_{boil}} - \frac{L_{vap}}{R}\frac{1}{T_*}$$

$$\therefore p = p_* e^{\frac{L_{vap}}{RT_*}} e^{-\frac{L_{vap}}{RT_{boil}}}$$

Expect a **Boltzmann Factor**
as the functional dependence of
pressure upon boiling temperature

$$\boxed{p \propto e^{-\frac{L_{vap}}{RT_{boil}}}}$$

Note L_{vap} is the *molar*
latent heat of vaporization

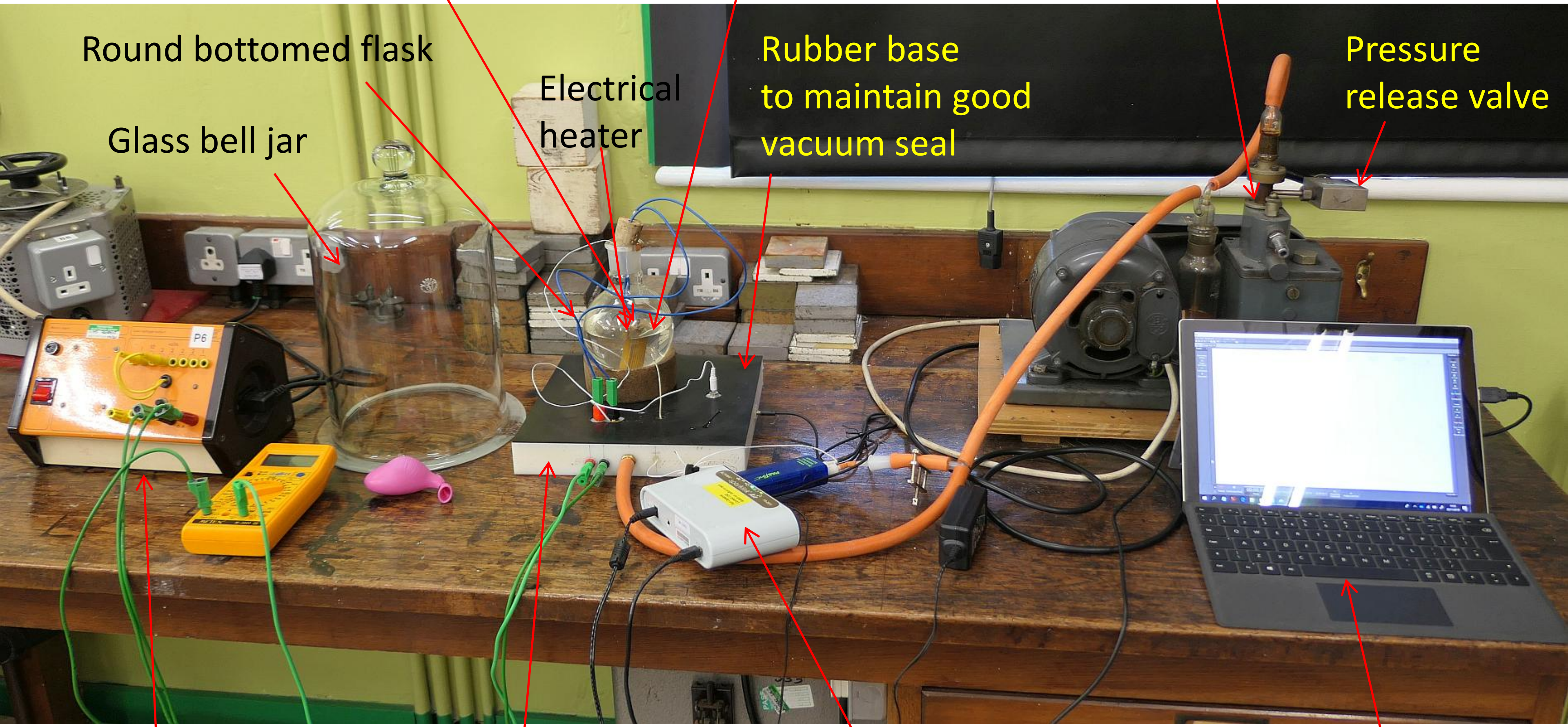
Linearized relationship:

$$\underbrace{\ln\left(\frac{p_*}{p}\right)}_{y} = \frac{L_{vap}}{R}\underbrace{\frac{1}{T_{boil}}}_{x} \underbrace{- \frac{L_{vap}}{R}\frac{1}{T_*}}_{c}$$

$$y = mc + c$$

$$m = \frac{L_{vap}}{R}, \quad c = -\frac{L_{vap}}{R}\frac{1}{T_*}$$

Equipment



About 400ml of water

Thermocouple in water

Vacuum pump

Round bottomed flask

Electrical heater

Glass bell jar

Rubber base to maintain good vacuum seal

Pressure release valve

12V DC power supply to electrical heater (about 4.8A)

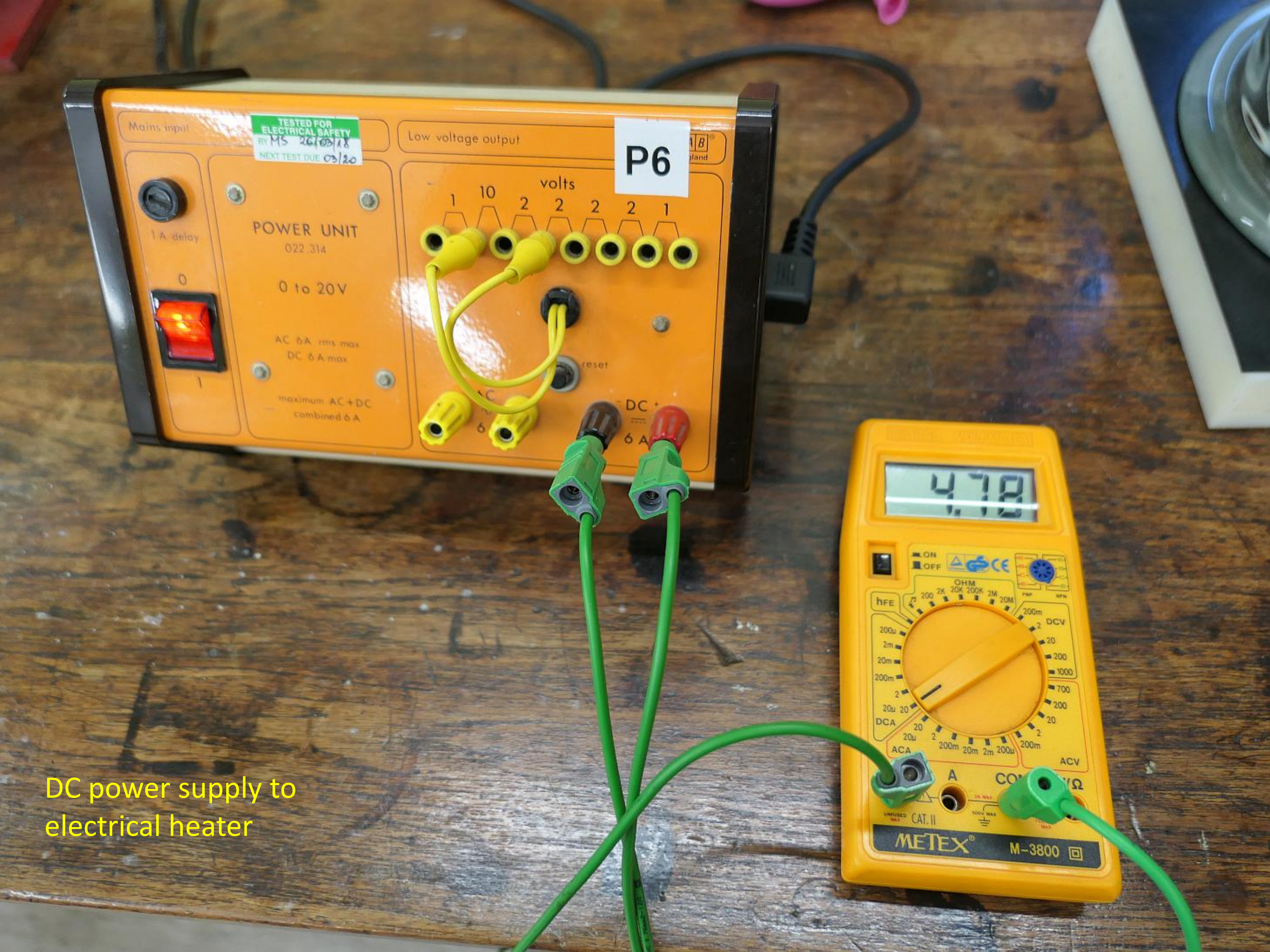
Pump valve, +/- power socket + 2x thermocouple connections drilled into plastic base

PASCO datalogger USB hub (pressure unit + 2x thermocouple connections)

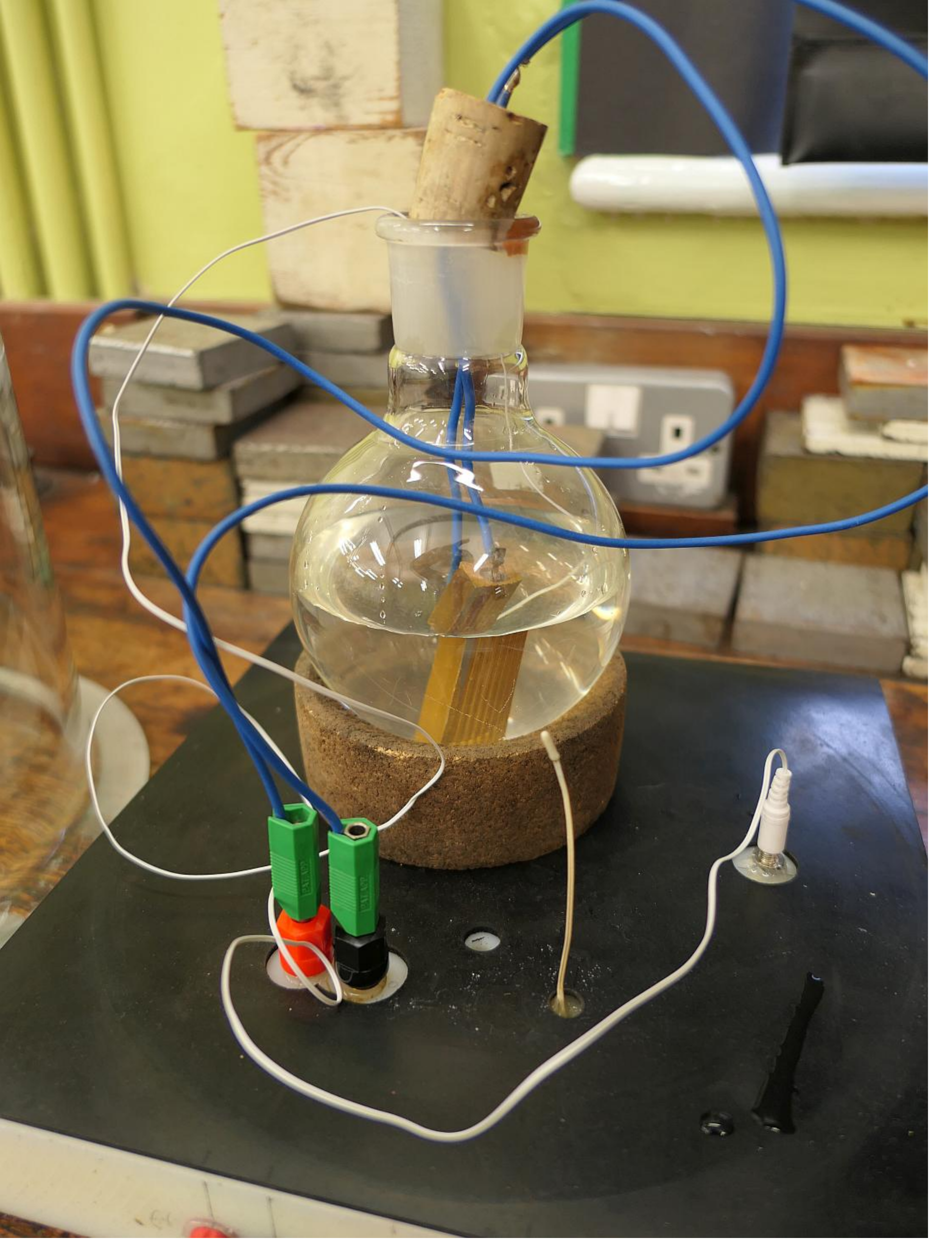
Laptop running CAPSTONE connected to USB hub

Vacuum pump, connected to bell jar. About 3% of atmospheric pressure is possible.

Turn pressure valve *slowly* to return air to bell jar between experiments.

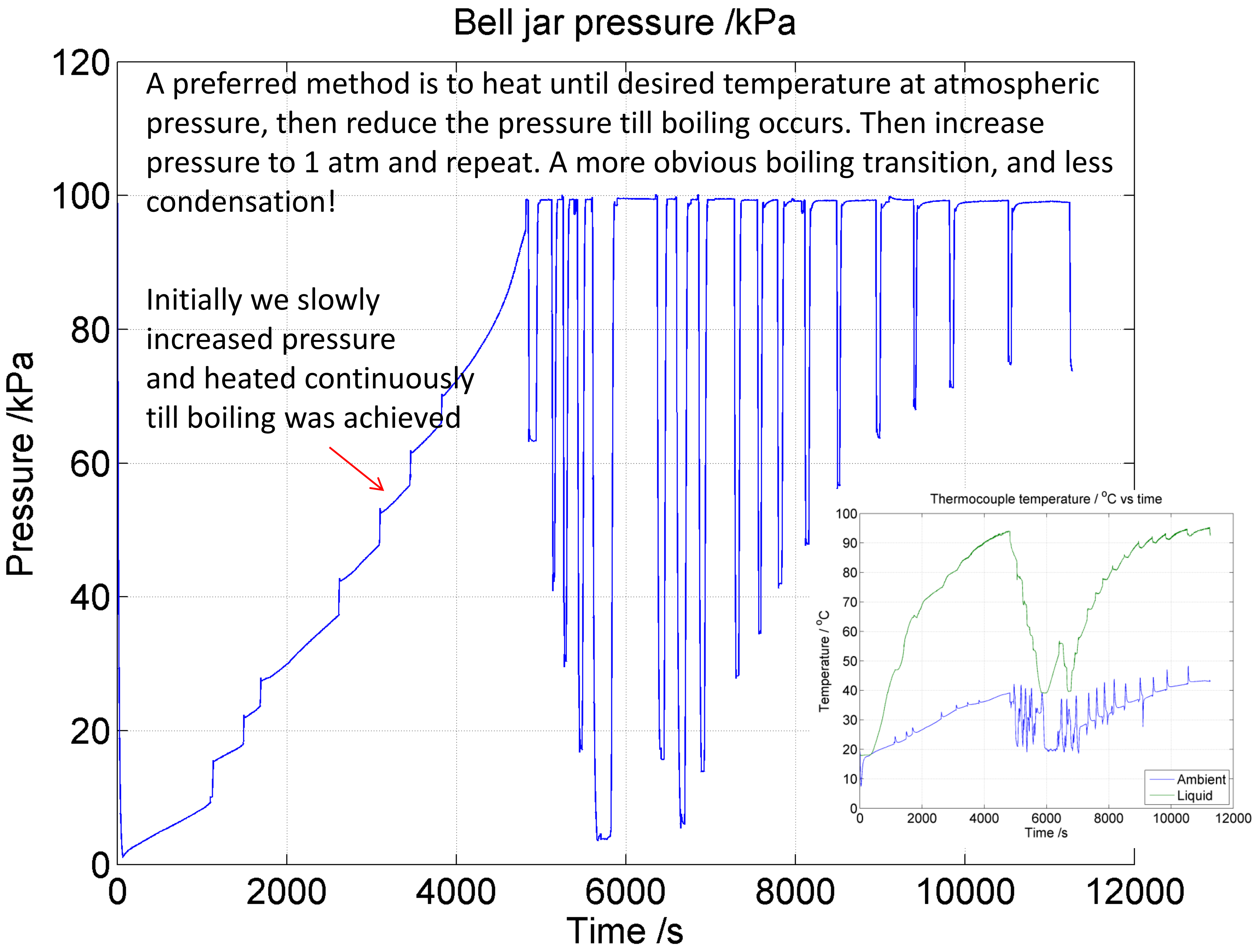


DC power supply to electrical heater



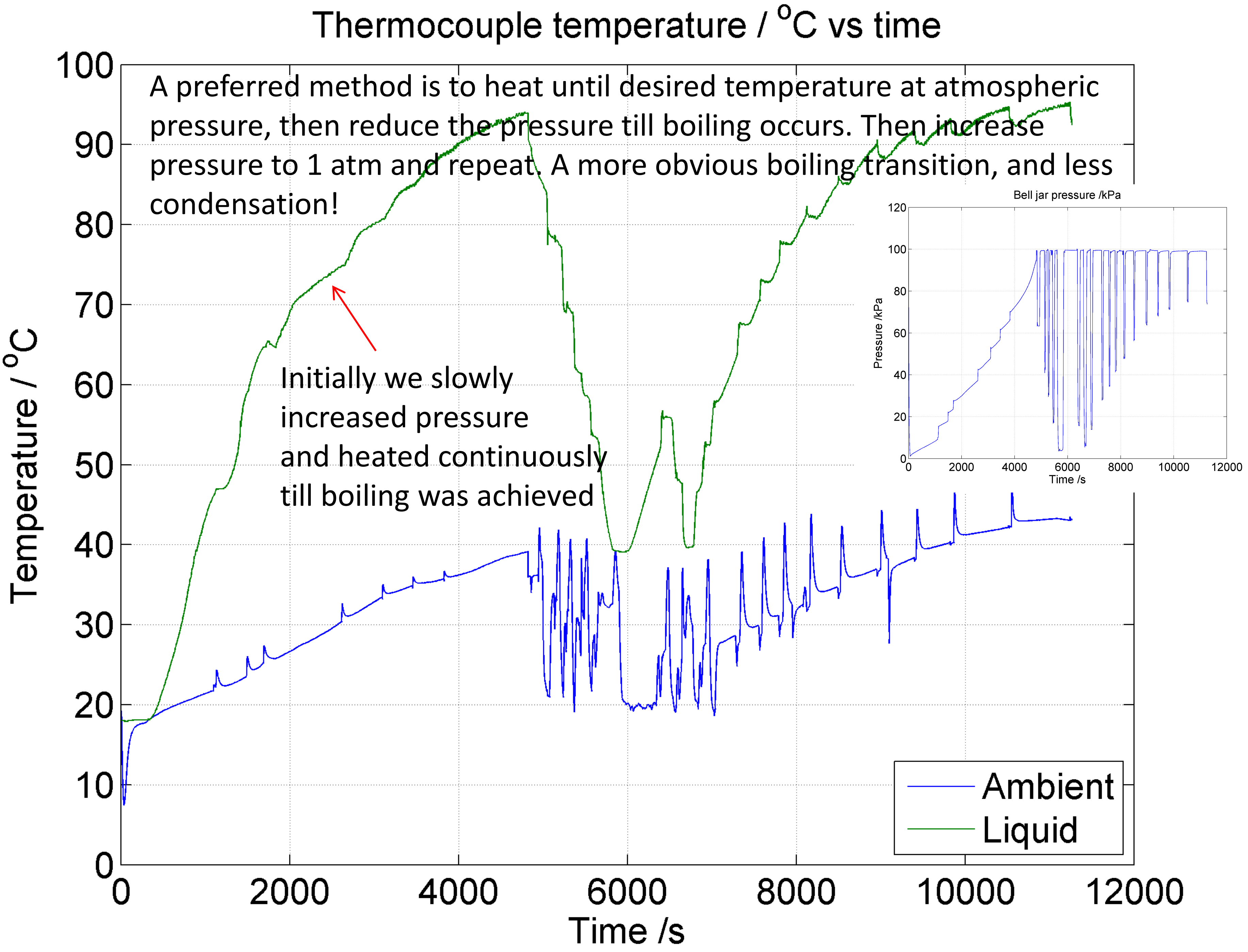
Heat water up to a desired temperature using electrical heater. (It is pretty slow, i.e about 10s per deg C, so you can leave it on)

Then pump out air till water spontaneously boils. At this point turn off the pump and record pressure and temperature using the datalogger display on the PC



A preferred method is to heat until desired temperature at atmospheric pressure, then reduce the pressure till boiling occurs. Then increase pressure to 1 atm and repeat. A more obvious boiling transition, and less condensation!

Initially we slowly increased pressure and heated continuously till boiling was achieved



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Excel analysis of raw data. Measurements were taken directly off the CAPSTONE display. Data rate was 10Hz for pressure and temperature. Perhaps 2H or 5Hz would have been easier to read the numbers? By eye, and error of about +/-0.3 ^{o}C and +/-0.2 kPa. i.e. too small to plot as an error bar.

Water temperature at boiling /degC	Bell jar pressure /kPa	Air temperature inside bell jar /degC	Notes	1000/Tboil (K^-1)	ln(P*/P)	Model P
40.7	6.5	28.9	** - explosive onset of boiling!	3.188	2.747	7.51
45.4	9.08	21.7	* Water at 18.1degC, reduce pressure to 2.7kPa, bell jar temp 17.6degC. Note spontaneous boiling, but ceased when turned pump off. Heated continuously (about 12V DC, 4.5A), and increased pressure in stages, and waited for boiling to commence	3.141	2.412	9.56
49.5	13.9	27.4	**	3.101	1.986	11.74
55.9	15.7	26.7	**	3.040	1.865	16.00
58.4	17.8	23.5	*	3.018	1.739	18.00
59.6	17.8	30.9	**	3.007	1.739	19.04
64.5	23.4	23.6	*	2.963	1.466	23.82
65.9	28.1	27.4	**	2.951	1.283	25.36
69.9	30.6	31.8	**	2.916	1.197	30.27
71.6	34.6	28.7	**	2.902	1.074	32.59
74.6	37.1	30.3	*	2.877	1.005	37.06
77.8	42	29.9	**	2.851	0.881	42.40
78	42.5	33.4	**	2.849	0.869	42.76
80.4	47.6	33.4	*	2.830	0.756	47.22
81	47.9	32.2	**	2.825	0.749	48.40
84.8	56.5	34.9	*	2.795	0.584	56.46
85.5	56.8	34.1	**	2.789	0.579	58.07
88.2	63.7	36.12	** Set temperature via heating or temperary immersion in a cold (or boiling) water bath. Atmospheric temperature, and bell jar periodically wiped of condensation. Then reduce pressure till boiling. Turn off pump, take measurement, increase pressure back to atmospheric and repeat. Easiest progression is to heat water to about 40degC, then start this process while heating constantly. Record boiling temp via lower pressure avery 5degC or so from 40degC.	2.769	0.464	64.63
88.6	63.8	36.7	**	2.765	0.463	65.65
88.8	65.8	35.7	*	2.764	0.432	66.17
90.5	68.5	38.2	**	2.751	0.391	70.71
91.7	71.3	40.2	**	2.742	0.351	74.07
93.2	75.2	42.3	**	2.731	0.298	78.47

* and ** denote the two experimental approaches undertaken. They are mixed as I have sorted the data by boiling temperature.

** is recommended.

Excel analysis

WATER BOILING POINT VS PRESSURE

A. FRENCH. P5 WINCHESETER COLLEGE. 1450-1800 22 Nov 2019.

errors: about +/- 0.3 degC and about +/-0.2Pa. (By eye from fluctuating readings).

Known data for water

P* /kPa	101.325
T* /K	373
Lvap (kJ/mol) at 30degC	43.78
R /J/mol/K	8.314

Water temperature at boiling /degC	**Bell jar pressure /kPa**	**Air temperature inside bell jar /degC**	**Notes**	**1000/Tboil (K^-1)**	**ln(P*/P)**	**Model P**
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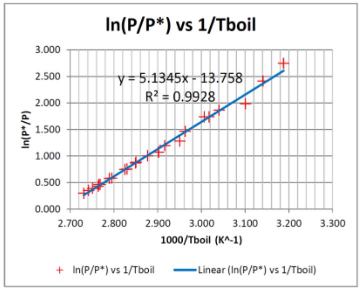
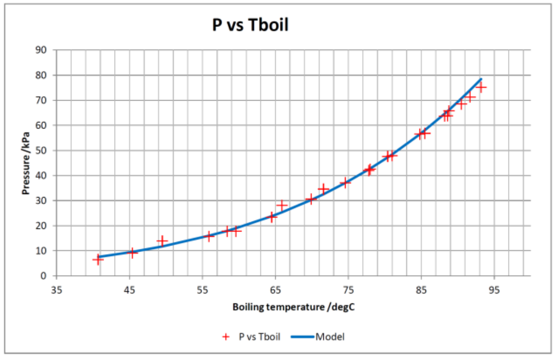


Lvap from gradient (/kJ/mol)

42.7

Lvap from intercept (/kJ/mol)

42.7



Clausius Clapeyron equation

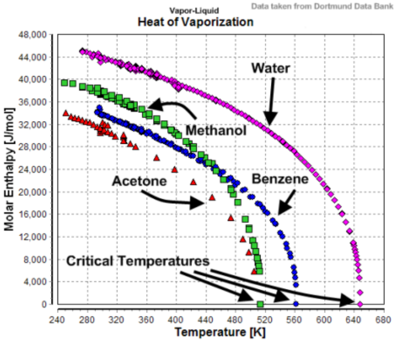
$$T_{boil} = \left(\frac{1}{T_*} - \frac{R}{L_{vap}} \ln\left(\frac{P}{P_*} \right) \right)^{-1}$$

$$\frac{1}{T_{boil}} = \frac{1}{T_*} - \frac{R}{L_{vap}} \ln\left(\frac{P}{P_*} \right)$$

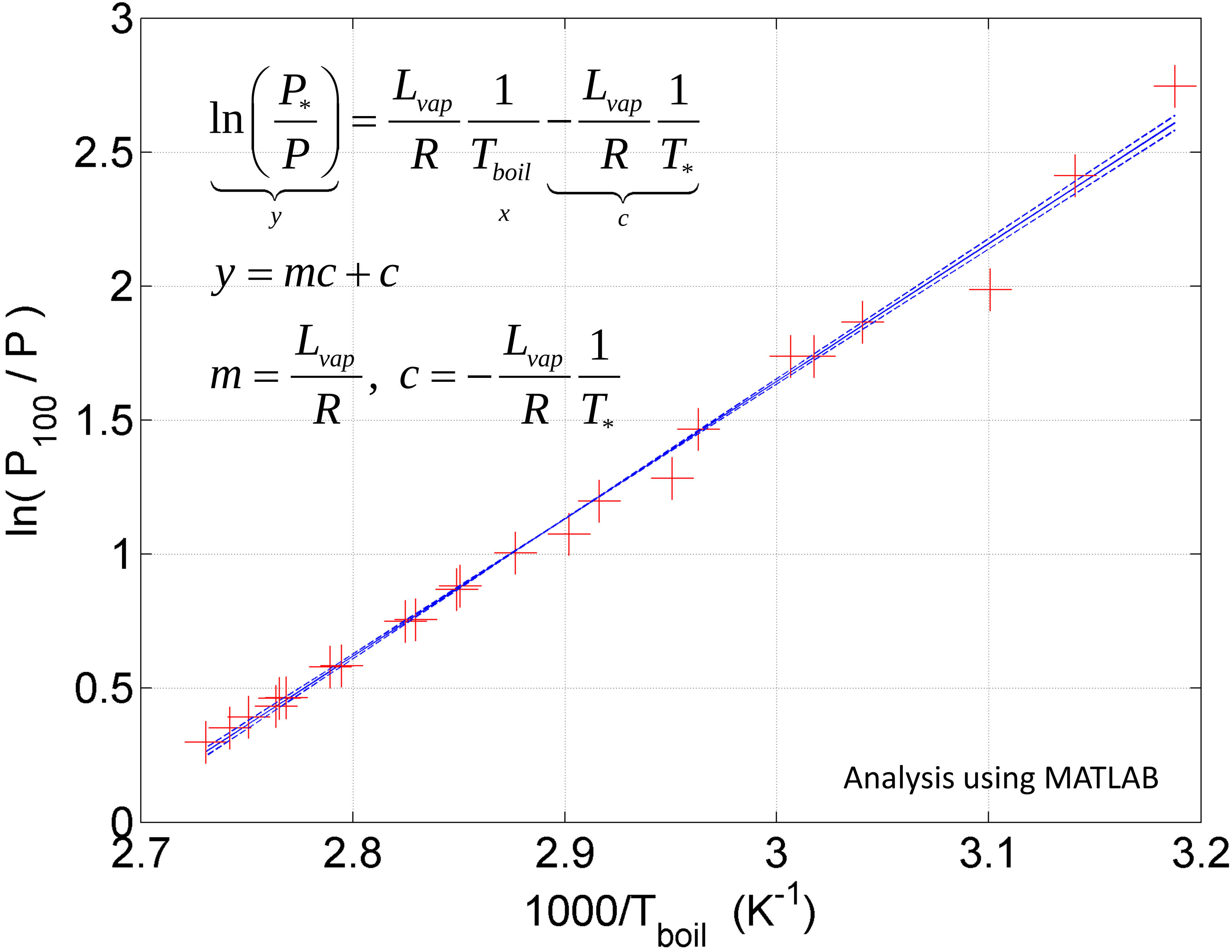
$$\frac{1}{T_{boil}} - \frac{1}{T_*} = \frac{R}{L_{vap}} \ln\left(\frac{P_*}{P} \right)$$

$$\therefore \ln\left(\frac{P_*}{P} \right) = \frac{L_{vap}}{R} \frac{1}{T_{boil}} - \frac{L_{vap}}{R} \frac{1}{T_*}$$

$$\therefore P = P_* e^{\frac{L_{vap}}{RT_*}} e^{-\frac{L_{vap}}{RT_{boil}}}$$


Data taken from Dortmund Data Bank

ln(P_{100} / P) vs 1/T_{boil}. L_{vap}= (42.7 +/-0.8) kJ/mol



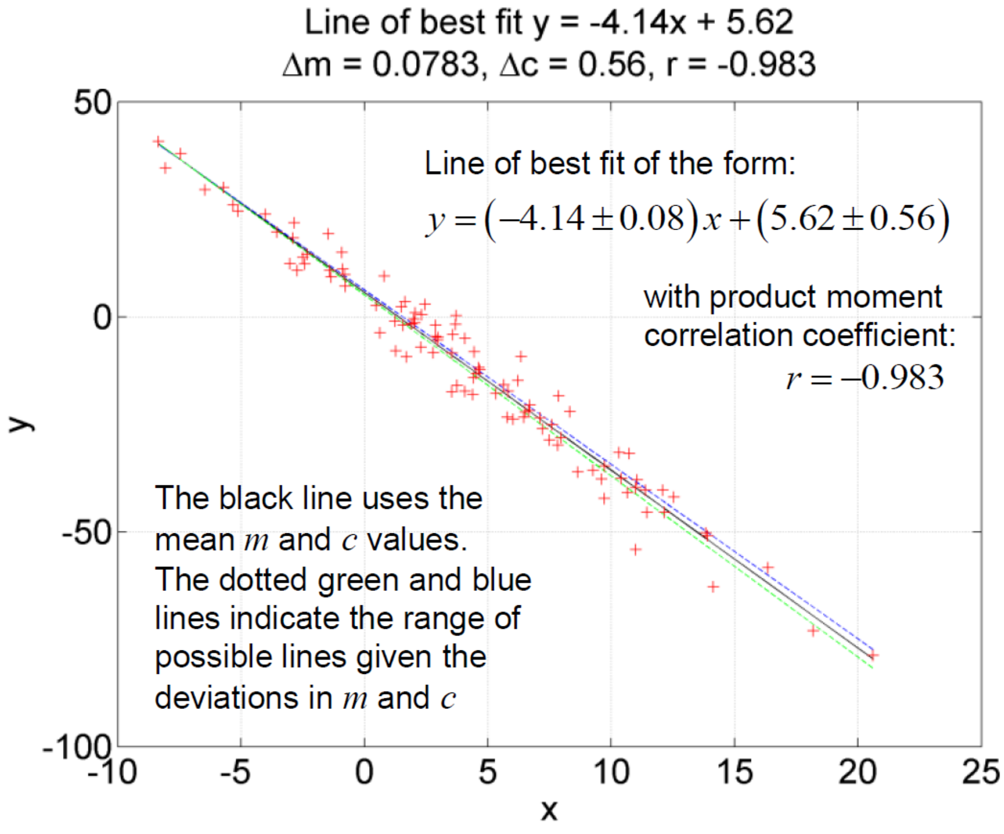
$$\underbrace{\ln\left(\frac{P_*}{P}\right)}_{y} = \frac{L_{vap}}{R}\underset{x}{\frac{1}{T_{boil}}} - \underbrace{\frac{L_{vap}}{R}\frac{1}{T_*}}_{c}$$

$$y = mc + c$$

$$m = \frac{L_{vap}}{R},\ c = -\frac{L_{vap}}{R}\frac{1}{T_*}$$

Analysis using MATLAB

$y = mx + c$ line of best fit recipe


Line of best fit y = -4.14x + 5.62

Δm = 0.0783, Δc = 0.56, r = -0.983

Line of best fit of the form:

$$y = (-4.14 \pm 0.08)x + (5.62 \pm 0.56)$$

with product moment correlation coefficient:

$$r = -0.983$$

The black line uses the mean m and c values. The dotted green and blue lines indicate the range of possible lines given the deviations in m and c

$$\bar{x} = \tfrac{1}{N}\sum_{i=1}^{N} x_i, \qquad \bar{y} = \tfrac{1}{N}\sum_{i=1}^{N} y_i,$$

$$\overline{x^2} = \tfrac{1}{N}\sum_{i=1}^{N} x_i^2, \qquad \overline{y^2} = \tfrac{1}{N}\sum_{i=1}^{N} y_i^2$$

$$\overline{xy} = \tfrac{1}{N}\sum_{i=1}^{N} x_i y_i$$

$$V[x] = \overline{x^2} - \bar{x}^2, \quad V[y] = \overline{y^2} - \bar{y}$$

$$\text{cov}[x,y] = \overline{xy} - \bar{x}\bar{y}$$

$$c = \bar{y} - m\bar{x}$$

$$m = \frac{\overline{xy} - \bar{y}\bar{x}}{\overline{x^2} - \bar{x}^2} = \frac{\text{cov}[x,y]}{V[x]}$$

$$r = \frac{\text{cov}[x,y]}{\sqrt{V[x]V[y]}}$$

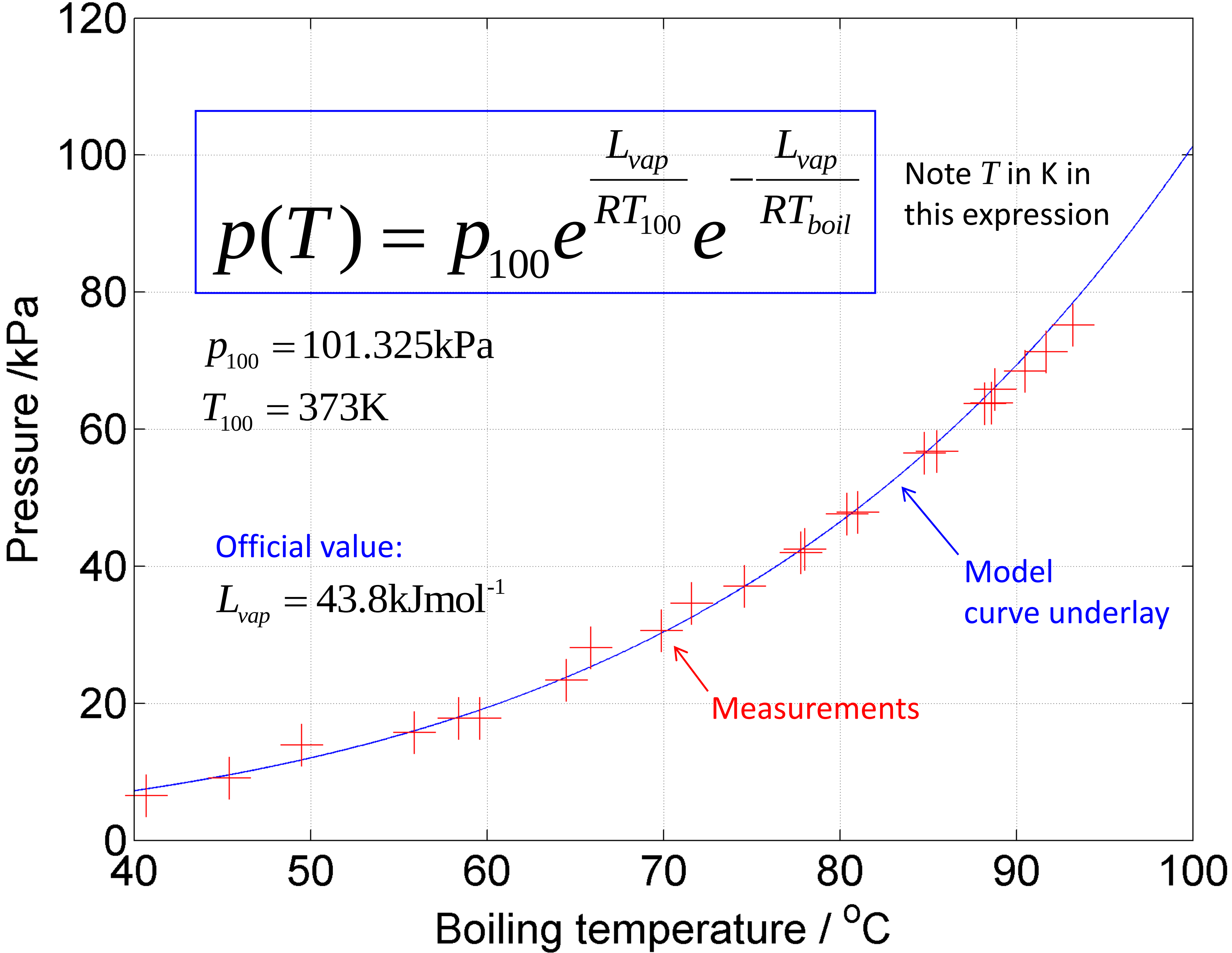
$$\Delta m = \frac{s}{\sqrt{N}}\frac{1}{\sqrt{V[x]}}$$

$$\Delta c = \frac{s}{\sqrt{N}}\sqrt{1 + \frac{\bar{x}^2}{V[x]}}$$

$$s = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}(y_i - mx_i - c)^2}$$

Errors in gradient and y intercept

Pressure vs boiling temperature. L_{vap} = (42.7 +/-0.8) kJ/mol



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Note *T* in K in this expression

$$p_{100} = 101.325\text{kPa}$$

$$T_{100} = 373\text{K}$$

Official value:

$$L_{vap} = 43.8\text{kJmol}^{-1}$$

Model curve underlay

Measurements