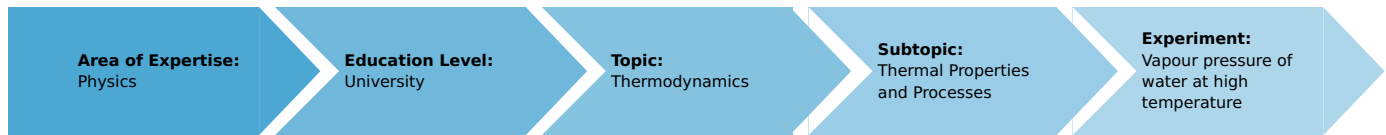


Vapour pressure of water at high temperature

(Item No.: P2340100)

Curricular Relevance



Difficulty



Difficult

Preparation Time



10 Minutes

Execution Time



30 Minutes

Recommended Group Size



2 Students

Additional Requirements:

- Distilled water

Experiment Variations:

Keywords:

boiling point, heat of vaporisation, Clausius-Clapeyron equation, Van't Hoff law, Carnot cycle

Overview

Short description

Principle

Water is heated in a closed pressure chamber; as much water vaporises as to make the pressure in the chamber correspond to the vapour pressure at the temperature at any time. The heat of vaporisation is determined at various temperatures from the measurement of vapour pressure as a function of temperature.



Fig. 1: Experimental set-up

Equipment

Position No.	Material	Order No.	Quantity
1	High pressure vapour unit	02622-10	1
2	Heating apparatus for glass jacket system	32246-93	1
3	Tripod base PHYWE	02002-55	1
4	Heat conductive paste, 50 g	03747-00	1
5	Boss head	02043-00	1
6	Lab thermometer, -10..+250C	38065-00	1
7	Pipette with rubber bulb, long	64821-00	1
8	Support rod, stainless steel, l = 250 mm, d = 10 mm	02031-00	1

Tasks

1. To measure the vapour pressure of water as a function of temperature.
2. To calculate the heat of vaporisation at various temperatures from the values measured.
3. To determine boiling point at normal pressure by extrapolation.

Set-up and procedure

Set up the experiment as shown in Fig. 1. Fill the high pressure steam unit with distilled water, with the aid of a pipette, ensuring that there are no air bubbles in the line leading to the pressure gauge.

Now screw the vessel together carefully (the lead seals may need replacing).

The unit is fastened with a bosshead and lays on the electric heater. Put the thermometer in the hole provided, which should be filled with heat conductive paste.

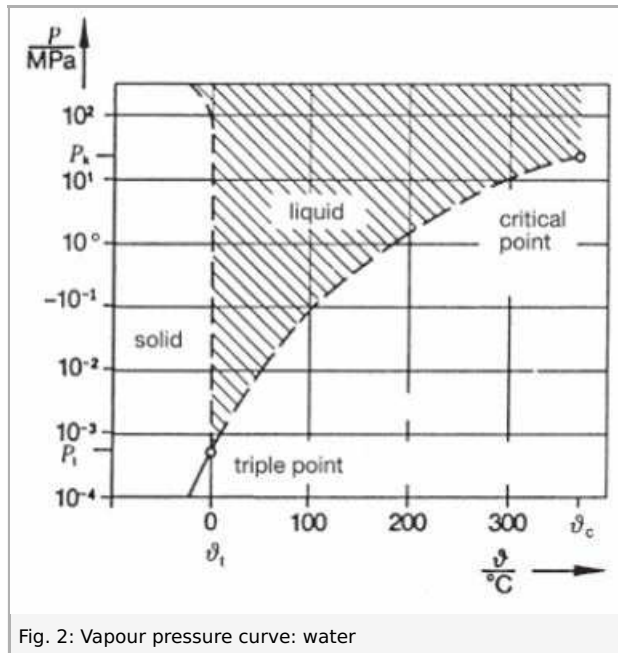
Heat the pressure vessel until the gauge reads 4 MPa 40 bar. Now switch off the heater and record the pressure and temperature as the equipment cools down.

Check the locking screws from time to time while the equipment is being heated and cooling down and tighten them if necessary.

Theory and evaluation

The thermal energy which must be taken up by one mole of liquid, to vaporise at constant temperature is called the molar heat of vaporisation Δ .

At a given temperature T resp. ϑ in degrees Celsius there is a vapour pressure p at which liquid and gaseous phase are in equilibrium (Fig. 2). When a liquid boils the vapour pressure is equal to the external (atmospheric) pressure.



The Clausius-Clapeyron differential equation

$$\frac{dp}{dT} = \frac{\Delta}{T(V_{\text{vap.}} - V_{\text{liq.}})} \tag{1}$$

where V_{vap} and V_{liq} are the molar volumes of vapour and liquid respectively and Δ is the heat of phase transition, applies here to the binodal curve bounding two phases.

The phase equilibrium when T and p are constant is governed by the function

$$G = U + pV - TS \tag{2}$$

where G = free enthalpy, U = internal energy, S = entropy.

Along the binodal curve

$$G_1(T, p) = G_2(T, p) \tag{3}$$

or in differential form

$$\left(\frac{\partial G_1}{\partial p} - \frac{\partial G_2}{\partial p}\right) dp + \left(\frac{\partial G_1}{\partial T} - \frac{\partial G_2}{\partial T}\right) dT = 0 \tag{4}$$

$$p_t = 6.1 \text{ hPa } \vartheta_t = 0.01 \text{ }^\circ\text{C},$$

$$p_c = 22.12 \text{ MPa } \vartheta_c = 374,2 \text{ }^\circ\text{C}.$$

With

$$\frac{\partial g}{\partial T} = -S \quad \text{and} \quad \frac{\partial g}{\partial p} = V \tag{5}$$

It follows from (3) that

$$(V_2 - V_1) dp = (S_2 - S_1) dT \tag{6}$$

The difference in entropy between the two phases can be expressed by the reversible latent heat of transformation

$$S_2 - S_1 = \frac{\Delta}{T} \tag{7}$$

(6) and (7) together give (1) for the binodal curve between the liquid and the vapour phase.

At low vapour pressures $p \ll p_c$, $V_{liq.} \ll V_{vap.}$ can be disregarded. In this range the vapour behaves very like an ideal gas and

$$V_{vap.} = \frac{RT}{p} \tag{8}$$

where $R = 8.3141 \text{ J/(K}\cdot\text{mol)}$, the universal gas constant.

From (1), therefore:

$$\frac{dp}{p} = \frac{\pi}{R} \cdot \frac{dT}{T^2} \tag{9}$$

Assuming Δ to be constant, by integrating we obtain the Van't Hoff equation

$$\ln p = -\frac{\Delta}{R} \cdot \frac{1}{T} + \text{const.} \tag{10}$$

The semi-logarithmic plot of the measured values (Fig. 3) shows an almost linear relationship between $\ln p$ and $1/T$. The heat of vaporisation changes with the temperature.

By fitting to a regression line in the ranges 190 °-250 °C and 150 °-190 °C, for example, we obtain the heat of vaporisation at 220 °C and 170 °C:

Heat of vaporisation (water)		
$\vartheta/^\circ\text{C}$	Molar $\Lambda/10^3 \text{ J mol}^{-1}$	Specific $\lambda/\text{J g}^{-1}$
220	36.2	2012
170	38.3	2126

By extrapolating the straight line in the low temperature range we can read off the boiling point of water at normal pressure, T_b . The measurements we have taken give:

$$\vartheta_b = 97^\circ\text{C}$$

The boiling point determined by extrapolation is too low because the curve for $\ln p = f(T)$ (Fig. 3) is slightly convex owing to differences in the heat of vaporisation.

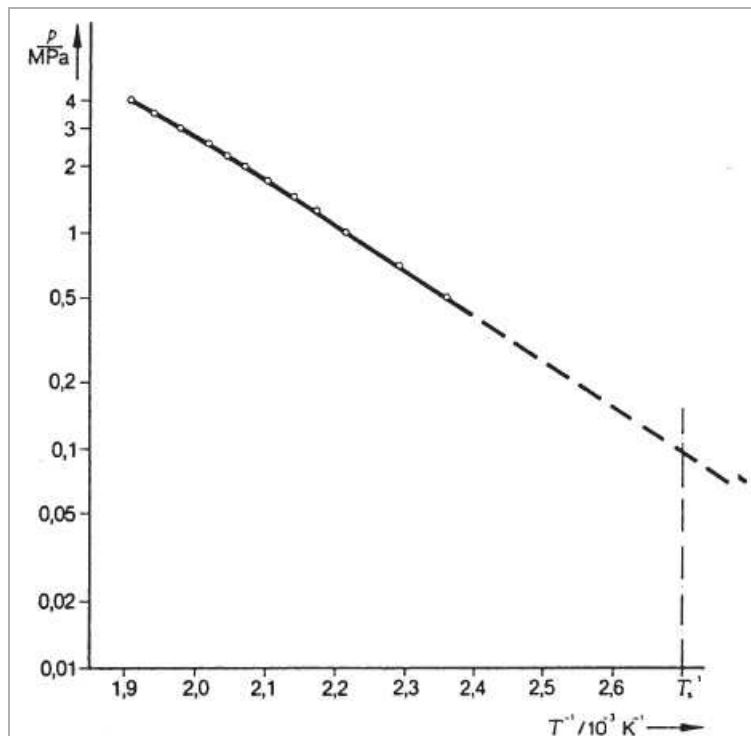


Fig. 3: Natural logarithm of vapour pressure p as a function of the reciprocal of the temperature ($1/T$): T_b = boiling point at normal pressure.

