Related topics

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

Principle and task

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.

Equipment

High pressure vapour unit	02622.12	1
Heat conductive paste, 50 g	03747.00	1
Heating apparatus	32246.93	1
Pipette, with rubber bulb, long	64821.00	1
Tripod base -PASS-	02002.55	1
Bosshead	02043.00	1
Support rod, stainl. steel, 250 mm	02031.00	1

Fig. 1: Experimental set-up for measuring vapour pressure as a function of temperature.

Problems

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 fastend 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 Λ.

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

$$\frac{dp}{dT} = \frac{\Lambda}{T\,(V_{vap.} - V_{liq.})} \qquad (1)$$

where $V_{vap.}$ and $V_{liq.}$ are the molar volumes of vapour and liquid respectively and Λ 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

$$G = U + pV - TS \qquad (2)$$

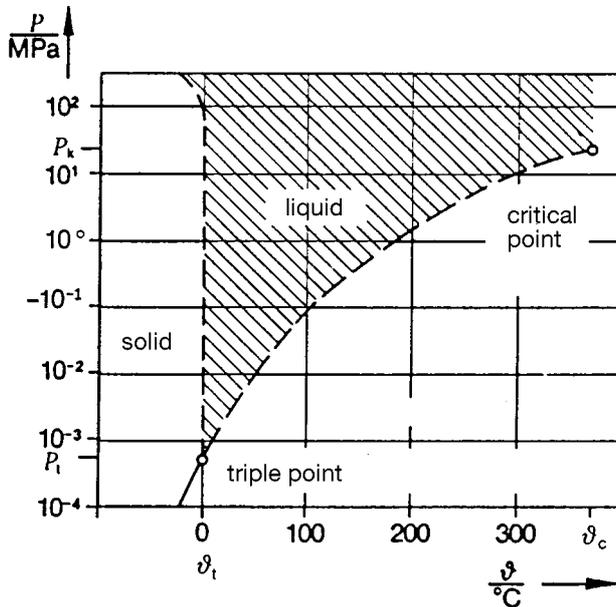where G = free enthalphy, U = internal energy, S = entropy.

Along the binodal curve

$$G_1\,(T,p) = G_2(T,p) \qquad (3)$$

or, in differential form

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

Fig. 2: Vapour pressure curve: water
p_t = 6.1   hPa, ϑ_t = 0.01°C,
pc = 22.12 MPa, ϑ_c = 374.2°C.

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)		
ϑ/°C	Molar $\Lambda/10^3$ J mol^{-1}	Specific λ/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:

$$\vartheta_b = 97°C$$

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.

With

$$\frac{\partial G}{\partial T} = -S \text{ and } \frac{\partial G}{\partial p} = V \qquad (1)$$

it follows from (3) that

$$(V_2 - V_1)\, dp = (S_2 - S_1)\, dT \qquad (6)$$

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

$$S_2 - S_1 = \frac{\Lambda}{T} \qquad (7)$$

(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

$$V_{vap.} = \frac{R \cdot T}{p} \qquad (8)$$

where R = 8.3141 J/K· mol, the universal gas constant.

From (1), therefore:

$$\frac{dp}{p} = \frac{\Lambda}{R} \cdot \frac{dT}{T^2} \qquad (9)$$

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

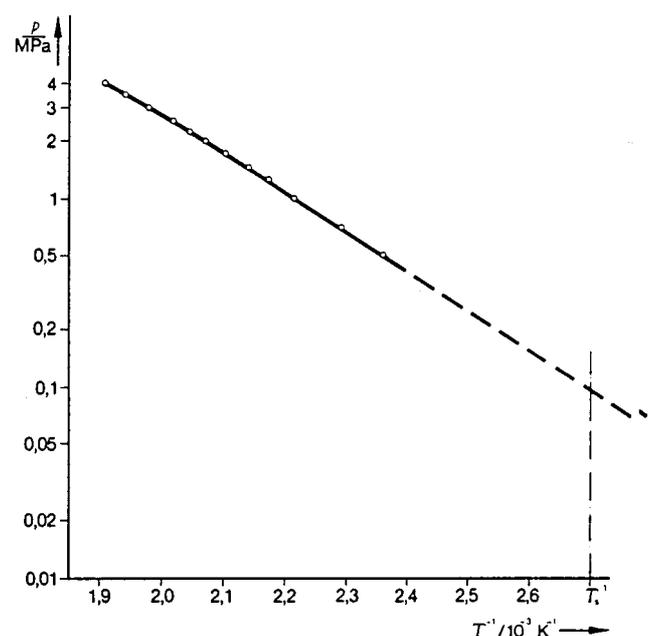$$\ln p = -\frac{\Lambda}{R} \cdot \frac{1}{T} + \text{const.} \qquad (10)$$

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.