Experiment no. 57

Vapor pressure of liquids (Clausius-Clapeyron equation)

Keywords:
Steam, vapor pressure of liquids, dynamic equilibrium, saturated steam, enthalpy of vaporization, vapor pressure curve, state diagram of water, supercooling, relative humidity, Clausius-Clapeyron' equation

Literature:
Atkins, “Physical Chemistry”
Christen, “Fundamentals of general and organic chemistry”
Gerthsen, Kneser, Vogel, “Physics”

Fundamentals:
Vapor is the gaseous phase of a substance that can be caused to condense by not too great a change in volume or temperature. If a closed vessel is partially filled with a liquid, the liquid evaporates until it is in dynamic equilibrium with its vapor. The vapor phase is then saturated. The saturated vapor pressure remains constant as the volume of the saturated vapor changes (i.e. it does not follow Boyle-Mariotte's law!!). However, it is strongly dependent on the temperature and increases monotonically and at an accelerated rate with the temperature (see Fig. 1).

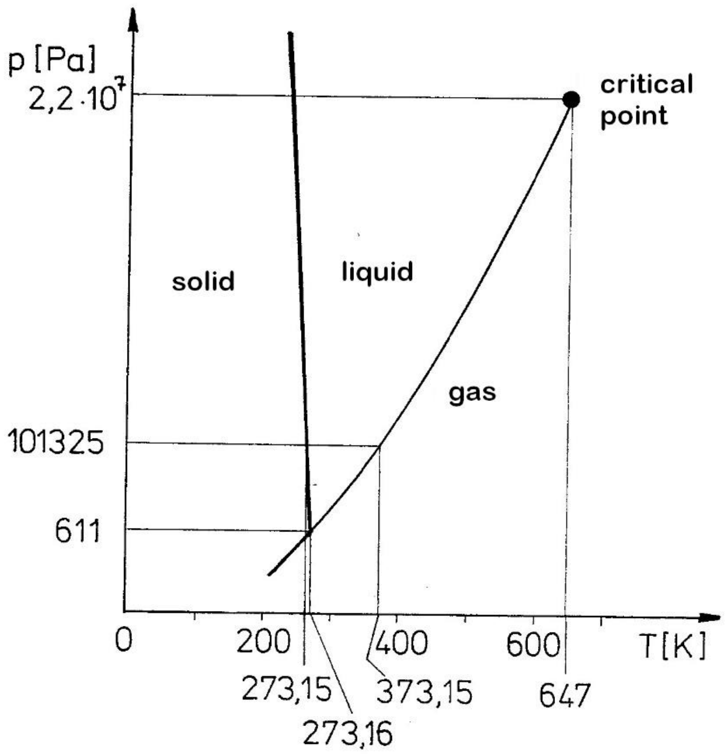

Fig. 1: State diagram of water (pressure axis not to scale)

From a molecular point of view, the process of vaporization consists of molecules leaving the surface of the liquid. To do this, they have to overcome mainly the cohesive forces and the external pressure. The corresponding energy is supplied to the liquid by the enthalpy of vaporization, which does not cause an increase in temperature, but only makes it possible for the molecules to leave the surface. This so-called latent heat supplied during evaporation is released again as heat of condensation during condensation.

The p,T relationship of a saturated vapor is described mathematically according to Clausius and Clapeyron. The form of the Clausius-Clapeyron equation integrated under approximations, August's equation, provides an exponential function of the form

$$(1) \quad p = \text{const.} \bullet \exp\left(- \Delta H_v / R \bullet 1 / T \right)$$

This equation makes the thermodynamically important quantity enthalpy of vaporization ΔH_v experimentally accessible. Equation (1) is only valid to a limited extent due to the physical simplifications on which it is based. However, since the vapor pressure curve is generally only required in a limited temperature range, its actual course can be reproduced with practically sufficient accuracy using Eq. (1).

Logarithmizing Eq. (1) results in:

$$(2) \quad \ln p = - \Delta H_v / R \bullet 1 / T + \text{const.}$$

$$y = m \bullet x + b$$

Eq. (2) thus corresponds to a straight line, the slope of which can be used to determine the enthalpy of vaporization ΔH_v. It is experimentally possible to cool a substance at a given pressure to a lower temperature than corresponds to the state of aggregation in which it is present. Small disturbances, such as sudden vibrations, the introduction of crystallization nuclei, etc., are then sufficient to immediately eliminate the unstable state of supercooling.

The relative humidity indicates the water vapor content of the air relative to the saturation vapor pressure at the respective temperature. At 100 % relative humidity, the air is saturated with water vapor.

Task:

The vapor pressure of water is measured between 0 °C and 20 °C and the enthalpy of vaporization is determined in this temperature range.

Experimental setup:

The experimental set-up is shown in Fig. 2. A mixture of ice, common salt and water is used as a cold bath to produce 0 °C in the measuring liquid. This of course has to be replaced after some of the water has frozen out and it has to be replaced by an ice-water mixture. Temperatures above 0 °C are produced by adding ice water to a bath of tap water.
A magnetic stirrer is used for better temperature equalization between the cold bath, measuring liquid and thermometer.

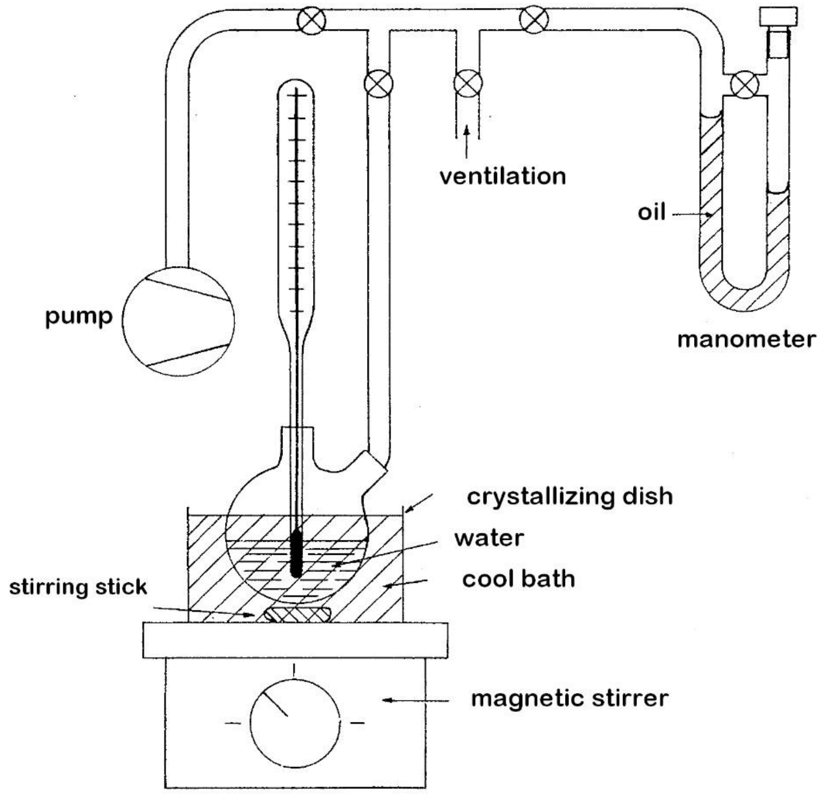

Fig. 2: Schematic diagram of the apparatus

Low pressures can be measured more accurately if a liquid with a much lower density is used as the manometer liquid instead of mercury. For a given pressure, the height difference Δh between the two manometer legs of the oil manometer is greater by the factor $\rho(Hg)/\rho(oil)$ than that of the mercury manometer (ρ = density):

(3) $$\frac{\Delta h\,(\ddot{O}l)}{\Delta h\,(Hg)} = \frac{\rho\,(Hg)}{\rho\,(\ddot{O}l)}$$

The oil used here has a density of 0.891 g•cm^{-3} at 20 °C; the density of mercury at 20 °C is 13.5462 g•cm^{-3}.

Procedure:

1) The two-necked flask is filled about halfway with (deionized) water and connected to the glass apparatus.

2) Most of the air is removed from the apparatus by briefly sucking it out.

3) An ice- salt mixture is produced in the crystallization dish ($t < -15°C$). The two-necked flask is immersed in the bath to above the water level and the magnetic stirrer is switched on.

4) After partial freezing of the water in the flask, the gas above the water is extracted again for about 15 s; then the connection to the pump is closed and the ice/salt bath is replaced by an ice/water mixture. When the vapor pressure in the apparatus no longer changes, the pressure and temperature are recorded.

5) About 6 cold baths between 0 °C and about 20 °C are prepared.
After setting the thermal equilibrium, the temperature in the flask and bath must be the same, the pressure and temperature are measured in each case.

Evaluation:

1) The differences in height measured with the oil manometer Δh are converted into mm Hg and mbar.

2) Two diagrams are drawn on graph paper:

(a) vapor pressure as a function of the corresponding absolute temperatures

b) Vapor pressure logarithmically as a function of the corresponding reciprocal absolute temperatures

3) Determine the enthalpy of vaporization of water in the measured temperature range from the graph 2b).

4) Discuss the accuracy of your measurements:

(a) What is the maximum error for the enthalpy of vaporization?

b) Is the literature value for the enthalpy of vaporization within the error limits of your own value?

Accessories:

Two-necked flask, thermometer, evacuable glass apparatus, oil manometer,

magnetic stirrer with stirring rod, 2 thermometer, wooden rod, Dewar flask