

## PRESSURE OF SATURATED VAPOR

OBJECT: To study the relationship between the temperature and pressure of saturated water vapor.

METHOD: The pressure in a spherical flask containing water is reduced by means of an aspirator. The boiling temperature is read directly from a thermometer and the pressure is determined from manometer and barometer readings. From a series of such observations the relationship between the temperature and pressure of saturated water vapor is determined.

THEORY: The molecules of a liquid are held together by attractive forces (cohesion) and any molecule that escapes from the liquid must move against a retarding force. According to the kinetic theory of heat, the molecules of the liquid are in motion. Since the velocities of the molecules vary greatly in magnitude and are purely random in direction, some of the molecules have sufficient velocity to escape from the surface. This process by which molecules are transferred from the liquid phase to the vapor phase is called evaporation.
Assume that the cylinder, Fig. 1, contains only water and its vapor. When equilibrium is established the rate at which molecules escape from the surface is equal to the rate at which molecules return from the vapor to the liquid, and the: region above the liquid is said to be saturated with water vapor. If the average kinetic energy of the molecules is increased (by raising the temperature), a larger fraction of


Fig. 1. The cylinder contains water and its vapor.
the molecules in the liquid have sufficient energy to escape from the surface and the rate of evaporation is increased. This increased evaporation raises the density of the vapor (and hence the rate at which molecules return from the
vapor to the liquid) until equilibrium is again established. From this it follows that the density of saturated water vapor and, therefore, the pressure of saturated vapor increase as the temperature rises. In fact there are two reasons for the increase in pressure: the increase in the density of the vapor and the increase in the speed of the vapor molecules.
If, while the temperature remains constant, the volume occupied by the vapor is decreased by pushing down the piston $P$, the density of the vapor is momentarily increased. The rate at which the molecules return to the liquid is now greater than the rate at which they leave, and the density of the vapor decreases until equilibrium is again established. This new equilibrium state is realized almost immediately and in this new equilibrium condition the density and pressure of the vapor are the same as before. Decreasing the volume merely changes water from the vapor phase to the liquid phase; it does not change the density or pressure of the vapor. As the piston is withdrawn, liquid is changed into vapor; but until the liquid has all disappeared there is no change in the pressure or density of the vapor. It is obvious, therefore, that the values of the density and pressure of saturated water vapor depend only on the temperature.
If vaporization takes place below the surface of a liquid, the process is called boiling. The reader has noticed that when water in a glass beaker is "brought to a boil" over a Bunsen burner, bubbles of vapor form at the bottom of the beaker, start to rise, and collapse. The reasons for this behavior should be clear from the above discussion. At the bottom of the beaker the pressure of the saturated vapor is equal to the outside pressure tending to collapse the bubble, but as the bubble rises to the cooler part of the vessel the vapor pressure falls below the outside pressure and the vapor is converted into liquid. The outside pressure acting on a bubble is made up of three parts: the atmospheric pressure acting on the surface, the hydrostatic pressure of the water, and the pressure which is due to surface tension. When the whole beaker of water has been raised to the boiling temperature, the bubbles of vapor rise to the surface and the vapor escapes to the atmosphere. The water is boiling. Since the temperature of the boiling liquid depends upon the depth, if an accurate determination of boiling temperature is desired the thermometer is not placed in the boiling liquid but is held in the saturated vapor above the liquid. The boiling temperature of a liquid is defined as the temperature of the saturated vapor above the boiling liquid. The boiling temperature may also be defined as the temperature at which the pressure of the saturated vapor is equal to the applied pressure. The boiling point is the particular value of the boiling temperature when the pressure is one standard atmosphere.


Fig. 2. The Vapor Pressure Apparatus and auxiliary equipment.
APPARATUS: A vapor pressure apparatus, a manometer, a Bunsen burner (or electric heater), one thermometer graduated in fifths of a degree to $100^{\circ} \mathrm{C}$, one thermometer graduated in degrees, an aspirator, rubber tubing, two stopcocks (one of which is attached to a T-tube), and access to a barometer are required.
The vapor pressure apparatus and auxiliary equipment are illustrated in Fig. 2, and the arrangement of this apparatus is shown schematically in Fig. 3. An aspirator is connected to the system by means of the rubber tube connection at $A$. When the pressure has been sufficiently reduced the stopcock $S$ is closed, and the difference between the barometric pressure B and the pressure $p$ inside the closed system is read from the manometer $M$. If $\mathbf{p}, \mathbf{B}$ and the manometer reading $h$ are all expressed in centimeters of mercury, it follows that

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\begin{equation*}
p=B-h \tag{1}
\end{equation*}
$$

Cold water from a faucet flows into the condenser jacket J through the inlet tube land out the outlet tube O into the sink. The Bunsen burner $G$ causes the water in the glass vessel $V$ to boil. The vapor from the boiling water rises into the vertical tube C where it is condensed by means of the cold water in the condenser jacket J and flows back into V . The water jacket is necessary in order to stabilize the pressure inside the system. Unless the vapor is condensed as rapidly as formed, this pressure continues to increase and the boiling temperature rises. The temperature of the vapor in V is read from the thermometer T . The spherical reservoir E serves to "smooth out" small fluctuations in pressure so that the manometer reading is steady.
If, with the aspirator not operating, air is let into the system by opening the stopcock $S$, water may be drawn into the system. Some of this water may be pulled into the manometer in which case the water must be removed before the experiment is continued. This may be prevented by placing a T-tube equipped with stopcock $\mathrm{S}^{\prime}$ in the tube connecting $E$ and $M$ and always letting air into the system through $\mathrm{S}^{\prime}$.

PROCEDURE: Since it is important that the temperature of


Fig. 3. The arrangement of the apparatus.
the water flowing through the condensing jacket J remain fairly constant, the faucet should be opened and left open until the temperature of the issuing water becomes stable. While waiting for the temperature to become stable, read the barometer. Use rubber tubing to connect the inlet tube I to the tap and to carry the water from the outlet O to the sink. With the stopcock $S^{\prime}$ open, so that the pressure inside the system is atmospheric, place the Bunsen burner G under the vessel V and boil the water. The water should boil for several minutes before any observations are taken. To keep the boiling water from splashing on the thermometer, the Bunsen burner should not be placed directly under the center of vessel $\vee$ but somewhat to one side. After the water has boiled for some minutes, read the thermometer T. Close the stopcock $\mathrm{S}^{\prime}$ and, with the aspirator operating, open the stopcock $S$ until the manometer reading $h$ is about 5 cm and then close it. When the reading of the thermometer T has become steady, read the temperature $t$, the, height $R_{1}$ of the mercury in the left arm of the manometer, and the height $R_{2}$ in the right arm. Record observations in the manner indicated in Table I. Take a series of observations increasing h in steps of approximately 5 cm . It will be found that when $h$ equals 50 or 60 cm some difficulty is encountered owing to "bumping," and the pressure should not be reduced below this point. Most thermometers are calibrated with all of the mercury, including that in the stem of the thermometer, at the same temperature. If, as in this experiment, the temperature of the mercury in the exposed stem differs considerably from the temperature of the bulb, corrections must be applied. It can be shown that

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\begin{equation*}
\Delta t=0.00016\left(t-t^{\prime}\right) l \tag{2}
\end{equation*}
$$

where $\Delta t$ is the amount that must be added to the observed temperature $t, t^{\prime}$ is the temperature at the midpoint of the exposed thread of mercury, and $I$ is the length of the exposed column expressed in degrees. The constant 0.00016 is the difference between the coefficients of volume expansion of mercury and glass. Place a thermometer beside the accurate thermometer and read $t^{\prime}$. Make the necessary correction to each observed value of the boiling temperature $t$.
Read the barometer again at the end of the experiment and take the average of the two readings as the value of the atmospheric pressure.
Plot the curve which shows the relation between the pressure of saturated water vapor (ordinates) and the temperature of the vapor (abscissas).
If the instructor so directs, substitute a pressure pump for the aspirator and extend the experiment to pressures above atmospheric.

QUESTIONS: 1. Water is being boiled over a Bunsen burner. If the flame is turned up, it supplies more heat to the water but the temperature of the water is not raised. Explain.
2. A boiling teakettle contains practically no air. Explain.
3. What is meant by a pressure of one standard atmosphere?
4. Criticize the statement "You can't boil eggs on Pike's Peak."
5. It should be clear from the results of this experiment that the pressure in the closed system is everywhere the same and is equal to the pressure of saturated water vapor. Explain in detail why this is true.
6. Explain how the size of the bubbles of vapor affects slightly the reading of a thermometer placed in a boiling liquid.

TABLE I

| Boiling temperature ( ${ }^{\circ} \mathrm{C}$ ) |  | Manometer readings (cm) |  |  | Pressure p <br> (cm of mercury) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Observed | Corrected | $\mathrm{R}_{1}$ | $\mathrm{R}_{2}$ | h |  |
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