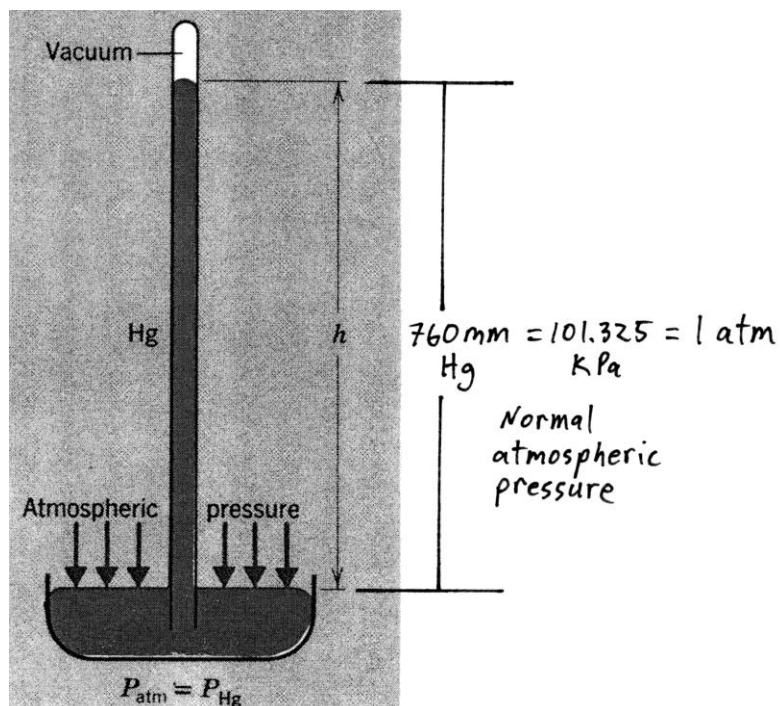


Chemistry Lecture #64: Atmospheric Pressure, Boiling Point, and Phase Diagrams

Atmospheric pressure is measured with a device called a *barometer*. The barometer was invented by Italian physicist Evangelista Torricelli (1608-1647). Torricelli took a glass tube that was open at one end and closed at the other end, and filled the tube with liquid mercury. He then inverted the tube and placed the open end into a bowl filled with mercury.



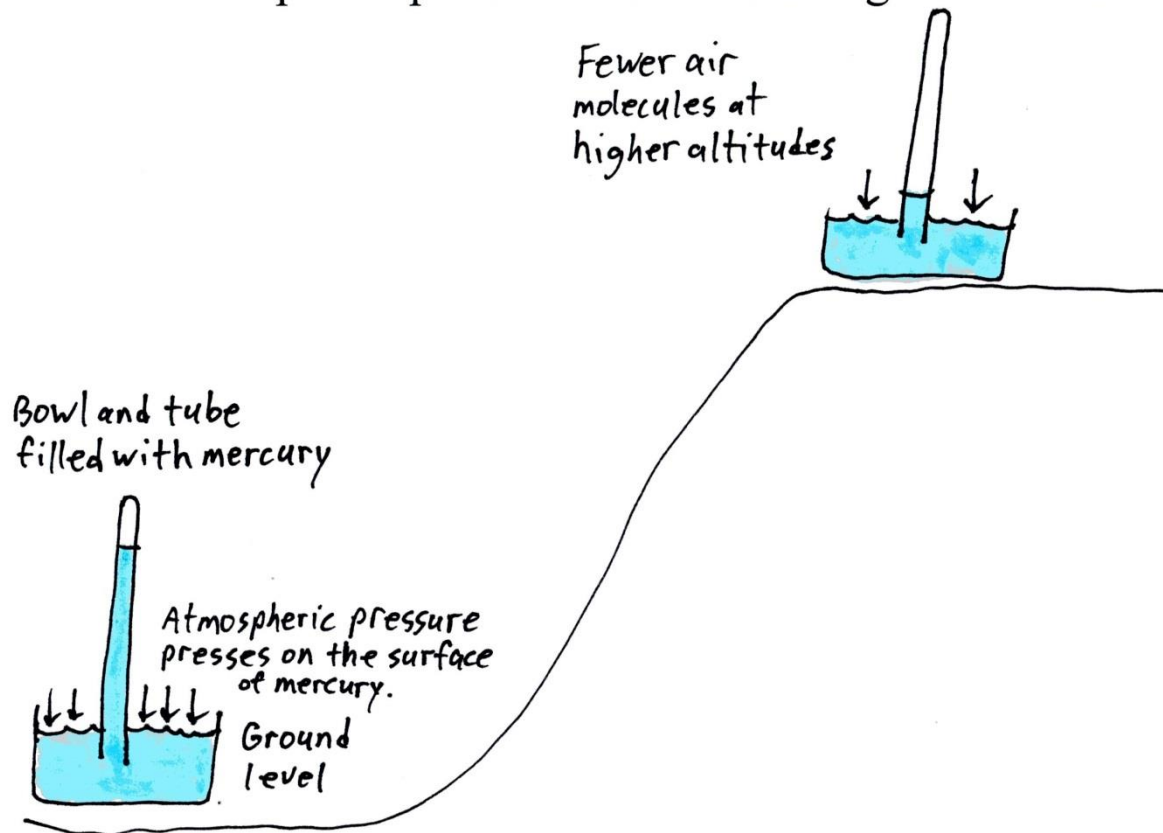
He noticed that the mercury in the tube did not completely spill into the bowl. The height of the mercury in the tube would fluctuate from day to day. Torricelli believed that atmospheric pressure exerted on the surface of the mercury in the bowl kept the mercury in the tube from spilling out. The height of mercury in the tube would go up and down as the atmospheric pressure went up and down.

Since the first barometers used mercury, atmospheric pressure is measured in mm Hg. In honor of Torricelli, sometimes the word *torr* is used instead of mm Hg. On normal, average day, the height of mercury in the tube will be 760 mm Hg or 760 torr. This is defined as *normal atmospheric pressure*. Pressure is also measured in *atmospheres (atm)* and *kilopascals (kPa)*.

$$760 \text{ mm Hg} = 1 \text{ atm} = 101.325 \text{ kPa}$$

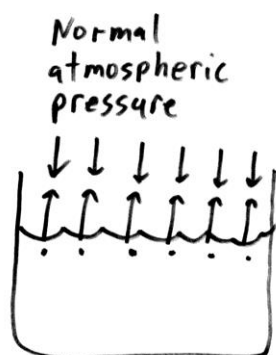
If a mercury barometer is taken from ground level to a higher altitude, the level of mercury will drop. At higher altitudes, there are fewer air molecules, and therefore less air pressure.

Atmospheric pressure decreases at higher altitudes.



Boiling occurs when the vapor pressure exerted by a liquid equals the atmospheric pressure. Since the atmospheric pressure at the top of a mountain is lower, liquids will boil at a lower temperature. For example, water normally boils at 100 degrees Celsius at ground level when the air pressure is 760 mm Hg. At the top of Mount Everest, however, the atmospheric pressure is about 250 mm Hg, and water will boil at 70 degrees Celsius.

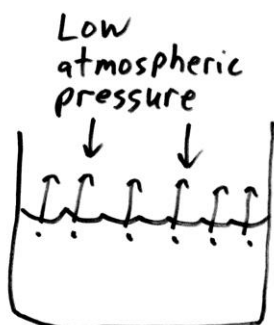
Boiling Point of H₂O



$$P = 760 \text{ mm Hg}$$

$$bp = 100^\circ\text{C}$$

Ground level



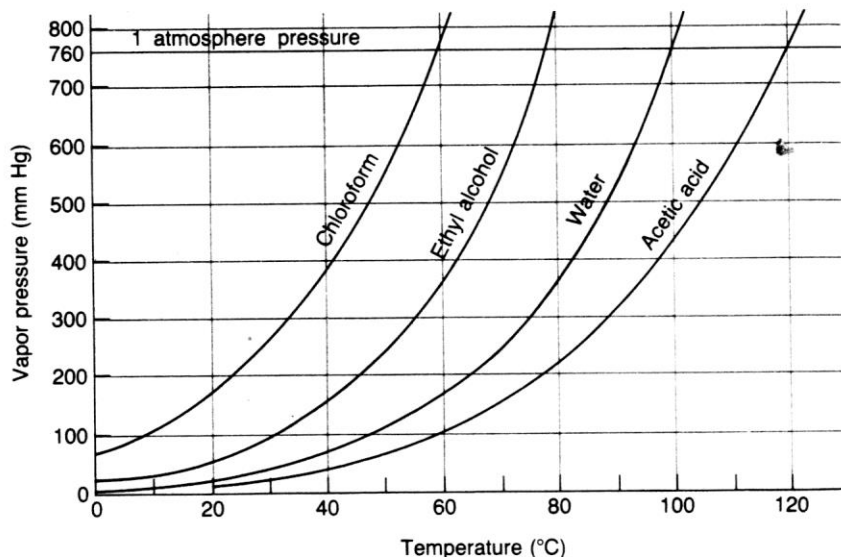
$$P = 250 \text{ mm Hg}$$

$$bp = 70^\circ\text{C}$$

Top of Mount Everest

At higher altitudes, foods cooked by boiling must be boiled for longer periods since the boiled water will be at a lower temperature. The next time you boil pasta, check the cooking directions and see if they give high altitude cooking instructions.

We can plot a graph of boiling temperature vs. atmospheric pressure for several different substances.



Notice that at 760 mm Hg, acetic acid boils at 120 degrees Celsius, water boils at 100 degrees, ethyl alcohol boils at about 78 degrees, and chloroform boils at 60 degrees Celsius. This shows that acetic acid has stronger intermolecular forces than water, but ethyl alcohol has weaker intermolecular forces. The hydrogen bonding that occurs in water and acetic acid makes the molecules stick together.

Atmospheric pressure not only affects the boiling point of liquids, but it also determines whether a substance exists as a solid, liquid or gas.

At high atmospheric pressure and low temperature, a substance will tend to exist as a solid.

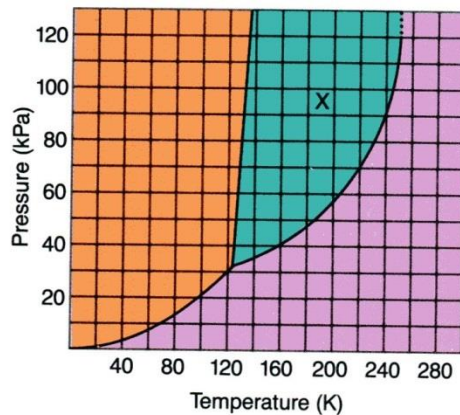
At moderate atmospheric pressure and moderate temperature, a substance will tend to exist as a liquid.

At low atmospheric pressure and high temperature, a substance will tend to exist as a gas.

Increasing temperature can cause a solid to turn into a liquid, and a liquid to turn into a gas.

Increasing atmospheric pressure can cause a gas to be compressed into a liquid, and a liquid to be compressed into a solid.

A phase diagram for a substance shows its physical state at different temperatures and pressures. Below is a phase diagram for an unknown substance "X." The pressure is in kilopascals (kPa) and the temperature is in Kelvins (K). The orange region represents the solid state. The blue region represents the liquid state. And the purple region represents the gas state.



At 40 K and 20 kPa, is the substance a solid, liquid or gas?

Answer: solid.

At 180 K and 60 kPa, is the substance a solid, liquid, or gas?

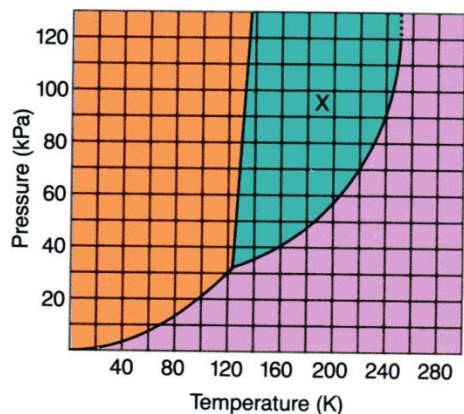
Answer: liquid

At 200 K and 30 kPa, is the substance a solid, liquid, or gas?

Answer: gas

At 130 K and 80 kPa, is the substance a solid, liquid, or gas?

Answer: both solid and liquid can exist. Melting or freezing can occur under these conditions.



At 100 K and 20 kPa, is the substance a solid, liquid or gas?

Answer: both solid and gas can exist. Sublimation can occur under these conditions.

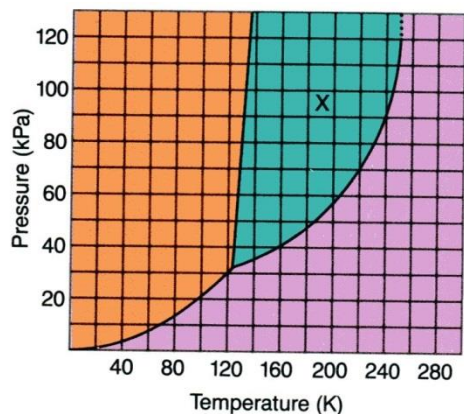
At 220 K and 70 kPa, is the substance a solid, liquid or gas?

Answer: both liquid and gas can exist. Boiling can occur under these conditions.

The *triple point* is the temperature and pressure where all 3 states of matter can exist. It's the point on the graph where all three lines intersect. At what temperature and pressure can solid, liquid, and gas exist?

Answer: about 135 K and 32 kPa

The *critical temperature* is the highest temperature the gaseous substance can reach and still be compressed into a liquid. Beyond the critical temperature, the gas cannot be compressed into a liquid. No amount of atmospheric pressure will be able to compress the gas. The critical temperature in the diagram is about 250 K (look for the dotted line on the top right). The pressure needed to compress a gas when it is at the critical temperature is the *critical pressure*, which is 120 kPa.



Normal boiling point and normal melting point are the temperatures needed to boil and melt the substance when the atmospheric pressure is 760 mm Hg (which is the same as 101.325 kPa or 1 atm).

What is the normal boiling point of the substance?

Answer: about 249 K

What is the normal melting point of the substance?

Answer: about 133 K