

Boiling Points of Liquids

In a container open to the atmosphere, boiling of a liquid will occur when the temperature is raised high enough. Vapour produced in the interior of the liquid results in the formation of a bubble. In order for a bubble to form, the vapour inside the bubble must be able to push back the atmosphere. This will not occur until a temperature is reached at which the vapour pressure is greater than the atmospheric pressure.

Therefore, the **boiling point** of a liquid is the temperature at which the vapour pressure is equal to the atmospheric pressure. Bubble formation will be impossible at temperatures below the boiling point because atmospheric pressure above the liquid will squeeze the bubble.

When the boiling point is reached, the vapour pressure equals the external pressure and therefore the bubble can survive, and rise to the top.

Since the boiling point of a liquid depends on the atmospheric pressure, and the atmospheric pressure varies daily, boiling point is not a constant, i.e. boiling point changes with external pressure. As pressure goes up, so does the boiling point (ex. pressure cooker). As the pressure goes down so does the boiling point (on the top of a mountain).

A **normal boiling point** is defined for the purposes of comparing liquid substances. The normal boiling point is the boiling temperature when the external pressure is 101.3 kPa.

Refer to the pressure – Temperature Graph for Water.

Relationship of Boiling Point to Enthalpy of Vaporisation and Intermolecular Forces

Molecules on the surface need a certain minimum amount of energy before they can escape from the attractive forces of the other surface molecules. This will depend on the strength of the intermolecular forces. Vaporisation is an endothermic process, as it requires the breaking of bonds. The amount of energy required for this phase change is known as the enthalpy of vaporisation, and it is directly proportional to the strength of intermolecular forces.

In general, ***the stronger the forces between the particles, the greater the enthalpy of vaporisation, the lower the vapour pressure, and hence higher the boiling point of the liquid.***

The boiling point and the heat of vaporisation are convenient measures of the strength of intermolecular forces. Boiling point reflects the kinetic energy that liquid molecules must have in order to overcome the intermolecular forces and escape into the gas phase. The energy required to vaporise one mole of a liquid is called the **molar heat of vaporisation, (ΔH_{vap})**.

Simple Distillation and Fractional Distillation

A volatile liquid can be separated from a non-volatile solute by simple distillation. A mixture of two miscible, volatile liquids, will not boil when the sum of the vapour pressures of the two components equals the external pressure.

The vapour will always contain a greater proportion of the more volatile component than the liquid phase does.

If the liquid contained an equal number of moles of two liquids, at the boiling point of the mixture, the more volatile component will be contributing more than 50 % of the vapour pressure. For example the vapour above an equimolar mixture of water and ethanol (b.p. = 78 °C) will contain more than 50 % ethanol, but it is not possible to obtain pure ethanol by simple distillation as there would still be significant amounts of water vapour. Such a mixture could however be separated by successive distillations.

Note: the greater the difference in boiling points the easier the separation.

In fractional distillation, the vapour from the liquid rises up the fractionating column, cools and condenses. It then runs down the column and meet shot vapours rising up, causing it to boil again.

Hence, as it rises up the column the liquid undergoes a number of vaporisations – condensation – vaporisation cycles, this being equivalent to having been distilled a number of times – thus the longer the column them more distillations.

If a suitable column is used, then the liquid distilling over will be the more volatile component of the mixture only, and eventually, at least in theory, the distillation flask will contain only the less volatile component.

Vapour Pressure and Boiling Points – Homework Questions

- How do the following physical properties depend on the strength of intermolecular forces?
 - surface tension
 - melting point
 - boiling point
 - vapour pressure
- Distinguish between the boiling point of a liquid and the normal boiling point of a liquid.
- What effect does increasing the temperature have on the vapour pressure of a liquid?
- Why does your skin feel cool when water evaporates from it?
- Why will you feel more uncomfortable on a more humid summer day than on a less humid day?
- Below are the vapour pressures of some common chemicals measured at 20 °C. Arrange them in order of (a) increasing intermolecular attractive forces, and (b) boiling points.

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|---------------|--------------|----------|
| Benzene | C_6H_6 | 10.6 kPa |
| Acetic acid | CH_3COOH | 1.55 kPa |
| Acetone | C_3H_6O | 24.5 kPa |
| Diethyl ether | $C_4H_{10}O$ | 58.5 kPa |
| Water | H_2O | 2.73 kPa |

- Why does rain often form when humid air is forced to rise over a mountain range?
- Explain how a pressure cooker works.
- Butane, C_4H_{10} , has a boiling point of $-5\text{ }^\circ\text{C}$. Despite this liquid butane can be seen sloshing inside a typical butane lighter, even at room temperature. Why isn't the butane boiling inside the lighter at room temperature?
- A CO_2 fire extinguisher is located on one of the outside walls of Colonel By school. During the winter months, one can hear sloshing sound when the extinguisher is gently shaken. Explain. Assume that the extinguisher has no leaks and that it has not been used.
- At $-35\text{ }^\circ\text{C}$, liquid HI has a higher vapour pressure than liquid HF. Explain.
- A mixture containing equal numbers of moles of hexane (b.p. $69\text{ }^\circ\text{C}$) and cyclohexane (b.p. $81\text{ }^\circ\text{C}$) is heated.
 - What determines the temperature at which a liquid boils?
 - What do the relative boiling points show about the relative strengths of the intermolecular forces in the two substances?
 - Would you expect this mixture to boil below $69\text{ }^\circ\text{C}$, between $69\text{ }^\circ\text{C}$ and $81\text{ }^\circ\text{C}$, or above $81\text{ }^\circ\text{C}$? Explain why.
 - How would you expect the composition of the vapour to compare with that of the liquid? Explain why this is so.
 - If the vapour is condensed and then further distilled a number of times, what will happen to the proportion of the two components in the distillate?
 - What separation technique depends on this principle?
 - Give one industrial application of the separation method.
- If intermolecular attractive forces are strong, then vapour pressure is _____, b.p. _____, if intermolecular attractive forces are weak, then vapour pressure is _____, b.p. _____.
- Why does H_2S have a lower boiling point than H_2Se ? Why does H_2O have a much higher boiling point than H_2S ?
- Give two examples of how you could use boiling under reduced pressure to your advantage?