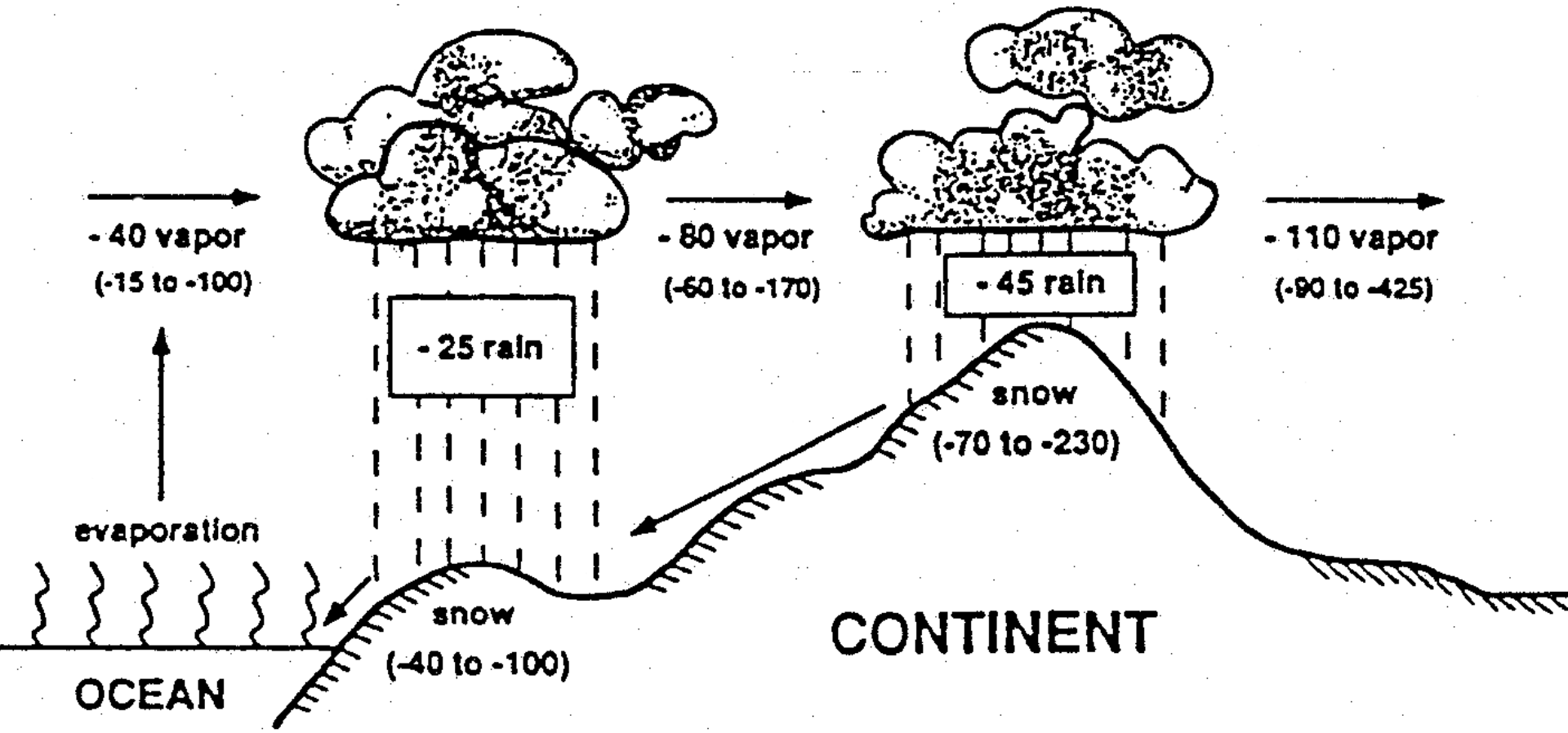
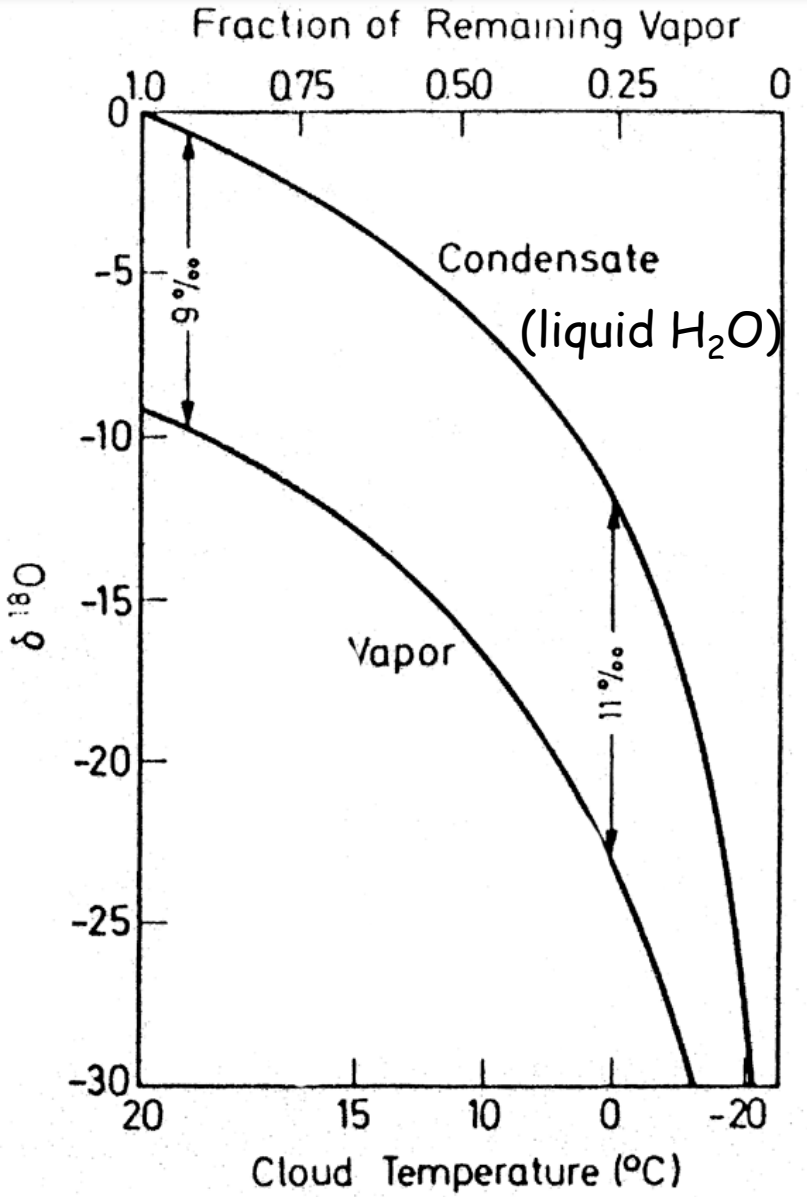
The Rayleigh type of isotope fractionation

UNIT 6

Rayleigh Fractionation

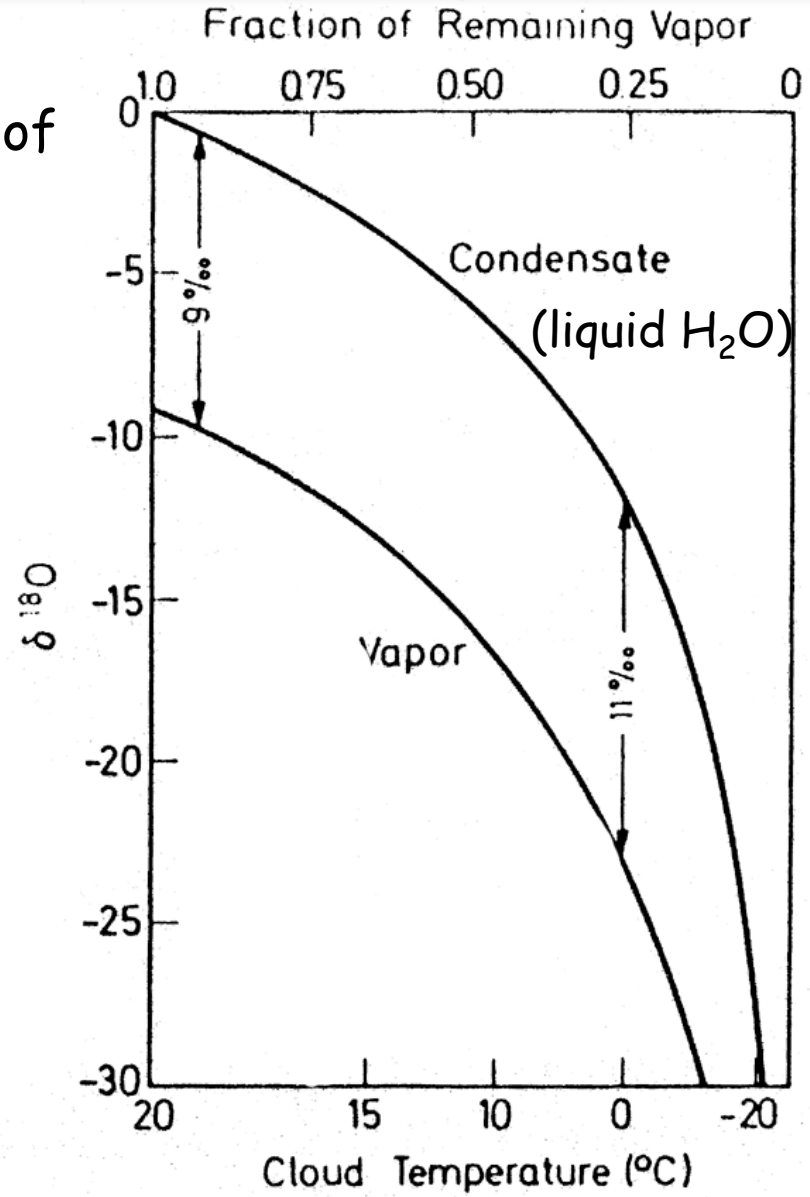


Rayleigh Fractionation



Rayleigh Fractionation

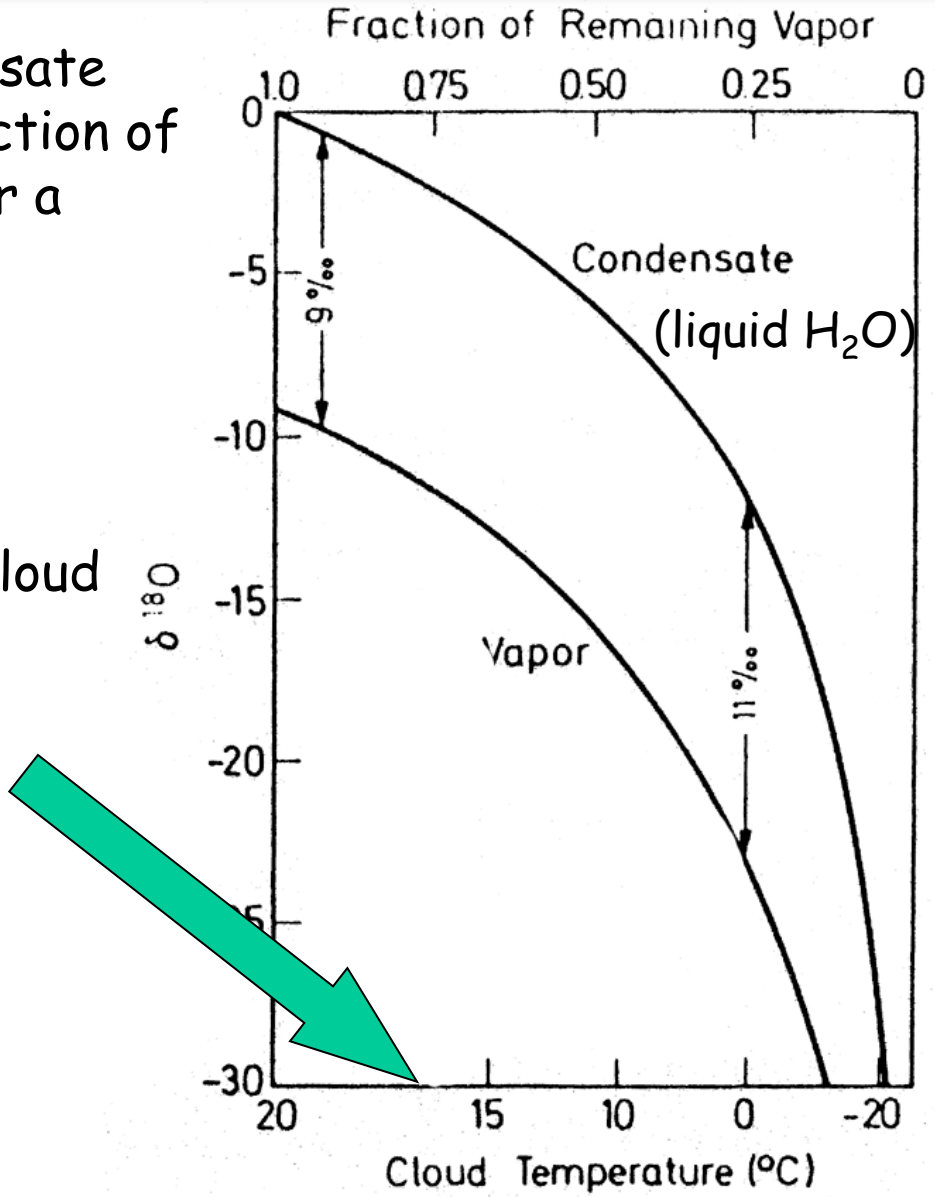
$\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the clouds for a Rayleigh process.



Rayleigh Fractionation

$\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the clouds for a Rayleigh process.

As evaporation proceeds, the temperature of the remaining cloud decreases.

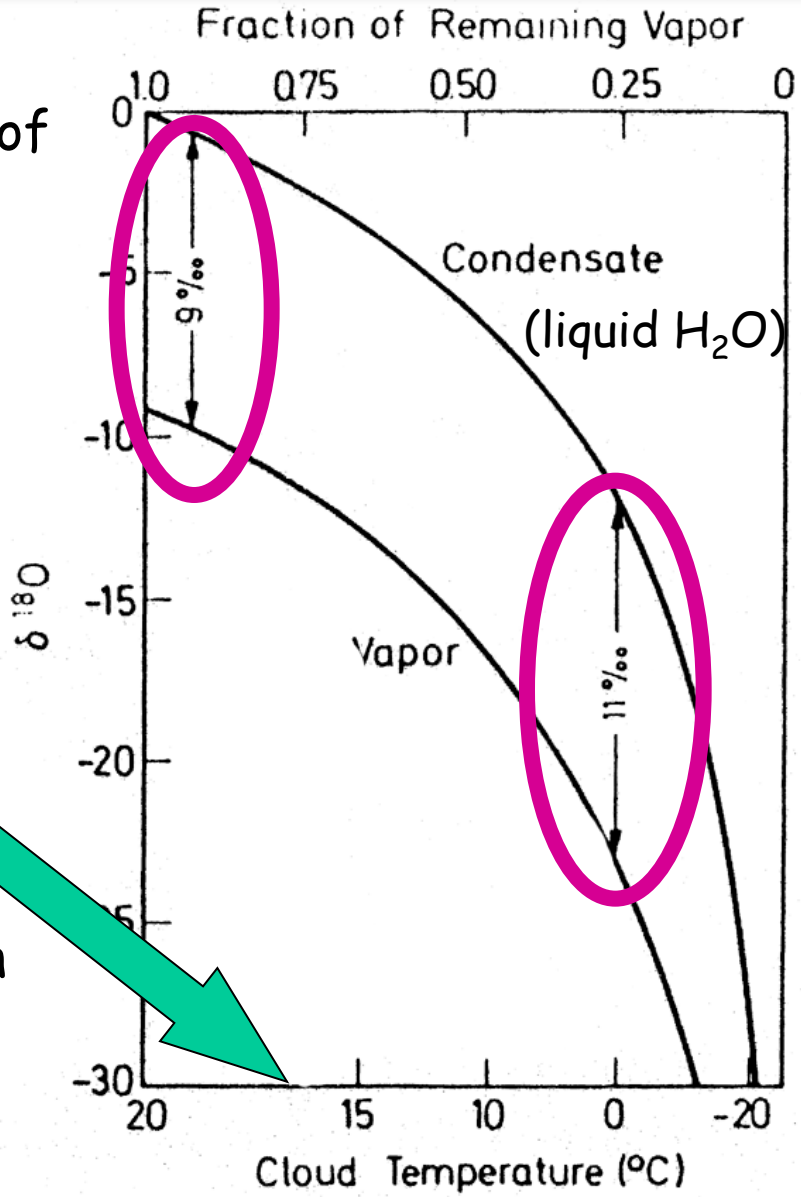


Rayleigh Fractionation

$\delta^{18}O$ in a cloud vapor and condensate plotted as a function of the fraction of remaining vapor in the clouds for a Rayleigh process.

As evaporation proceeds, the temperature of the remaining cloud decreases.

The increase in fractionation with the decreasing temperature is taken into account



Rayleigh Fractionation

Rayleigh distillation describes the observed patterns of ISOTOPE FRACTIONATION as a liquid pool evaporates – such as in cloud formation.

Rayleigh Fractionation

Rayleigh distillation describes the observed patterns of ISOTOPE FRACTIONATION as a liquid pool evaporates – such as in cloud formation.

Rayleigh distillation is an FRACTIONATION process either equilibrium or kinetic), which creates differences in δ values.

Rayleigh Fractionation

Rayleigh distillation describes the observed patterns of ISOTOPE FRACTIONATION as a liquid pool evaporates – such as in cloud formation.

Rayleigh distillation is an FRACTIONATION process either equilibrium or kinetic), which creates differences in δ values.

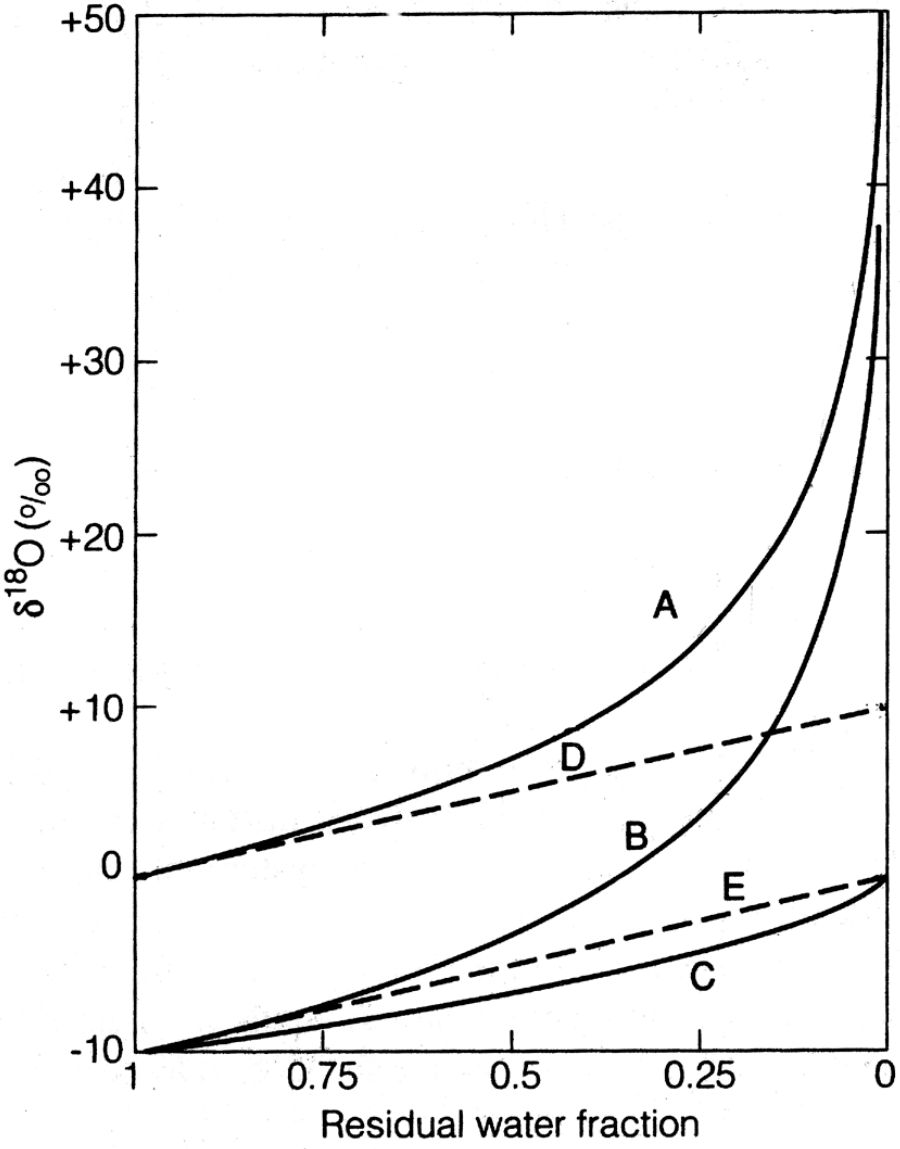
This fractionation is due to the different PHYSIO-CHEMICAL BEHAVIORS of the isotopes.

Rayleigh Fractionation

Rayleigh distillation describes the observed patterns of ISOTOPE FRACTIONATION as a liquid pool evaporates – such as in cloud formation.

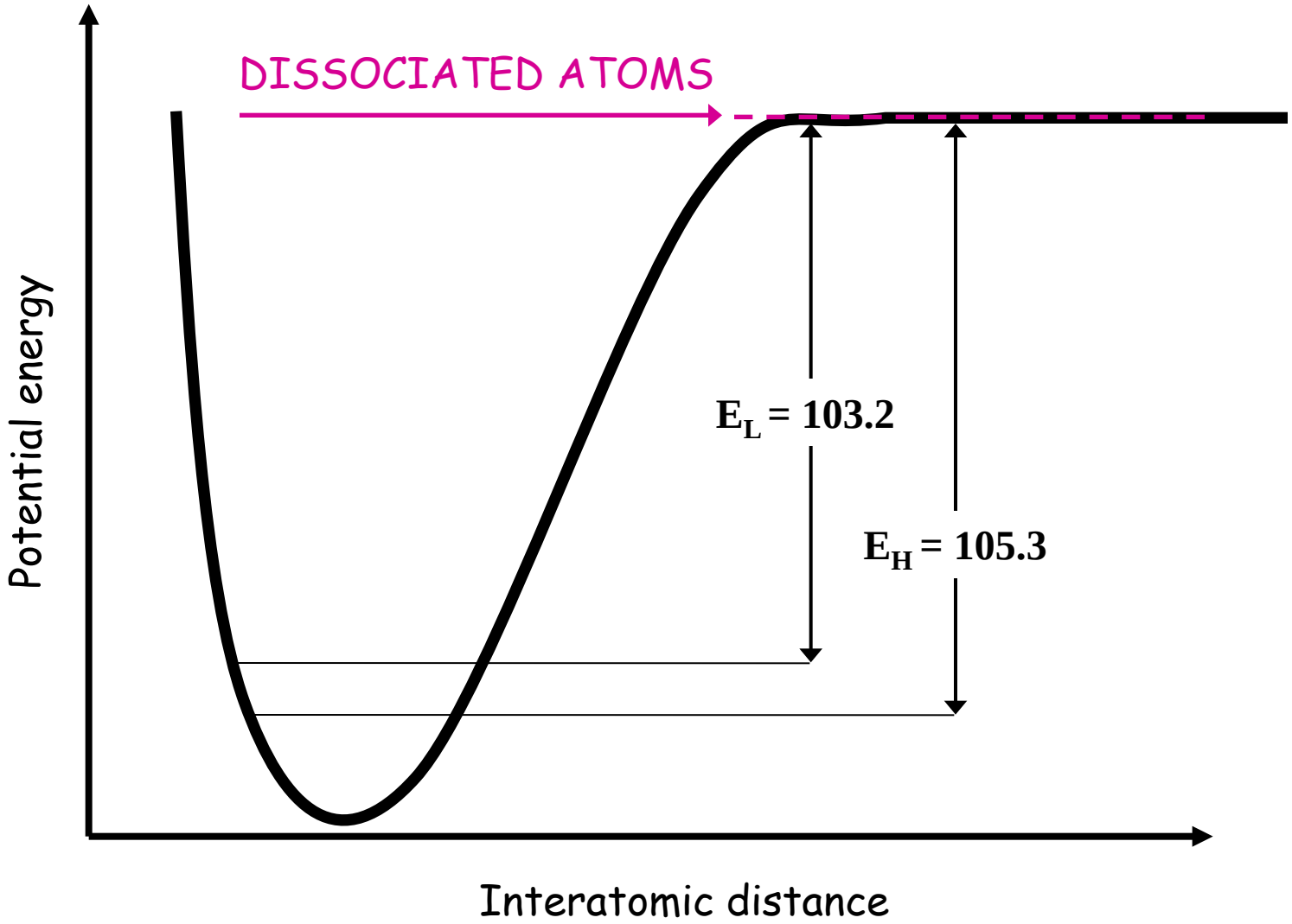
Rayleigh distillation is an FRACTIONATION process either equilibrium or kinetic), which creates differences in δ values.

This fractionation is due to the different PHYSIO-CHEMICAL BEHAVIORS of the isotopes.



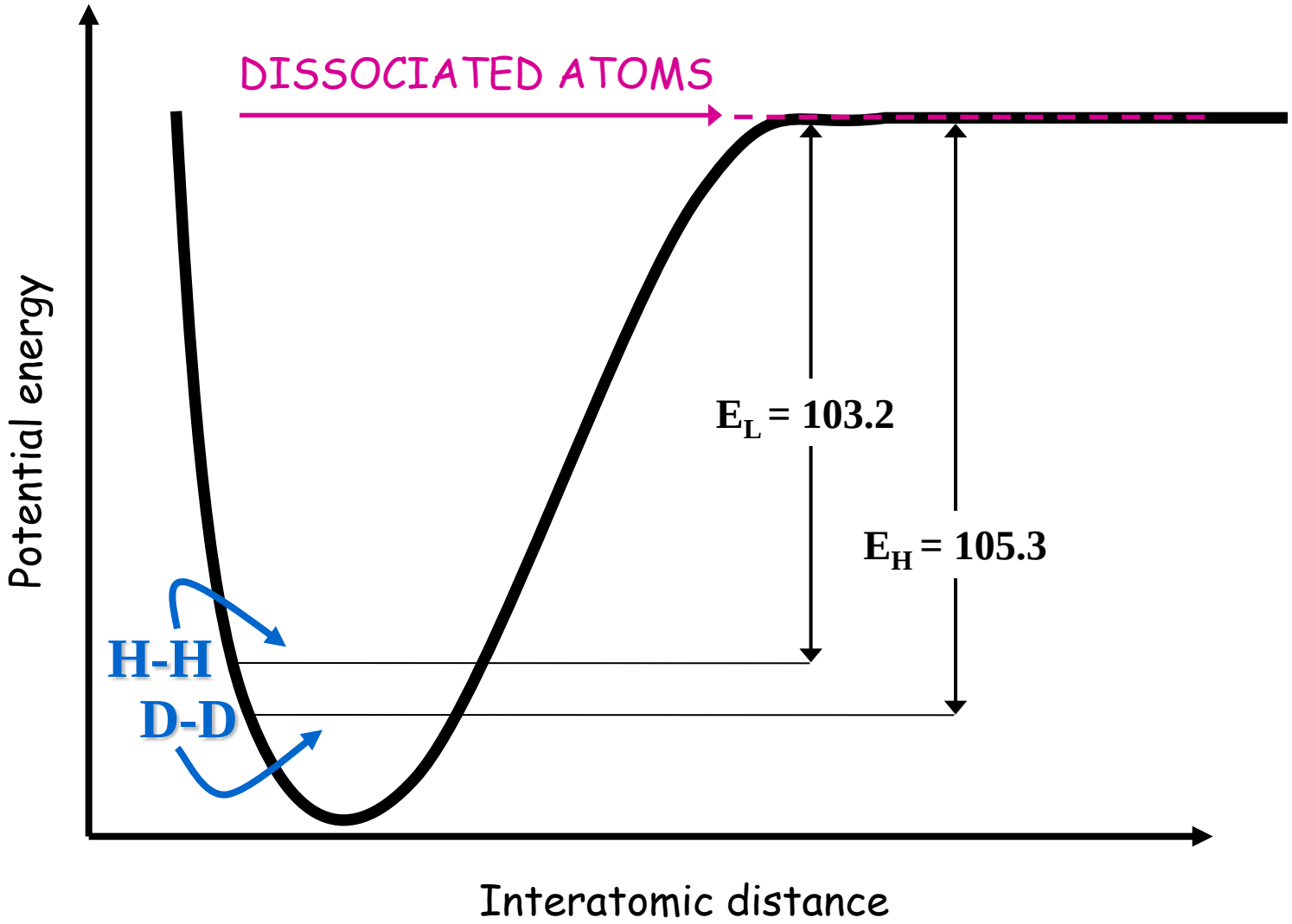
Rayleigh Fractionation

Why does $H_2{}^{16}O$ have a higher vapor pressure?"



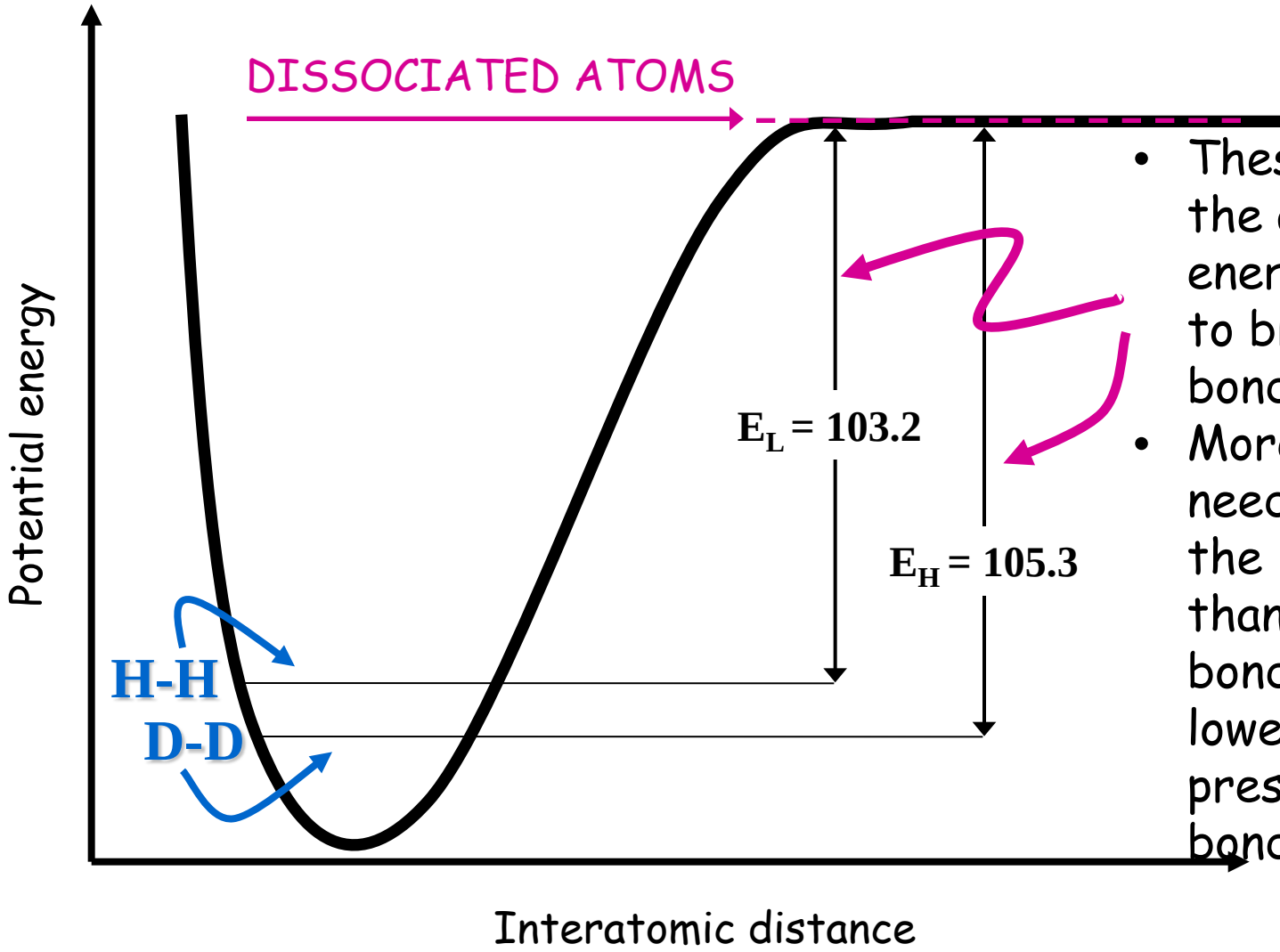
Rayleigh Fractionation

Why does $H_2{}^{16}O$ have a higher vapor pressure?"



Rayleigh Fractionation

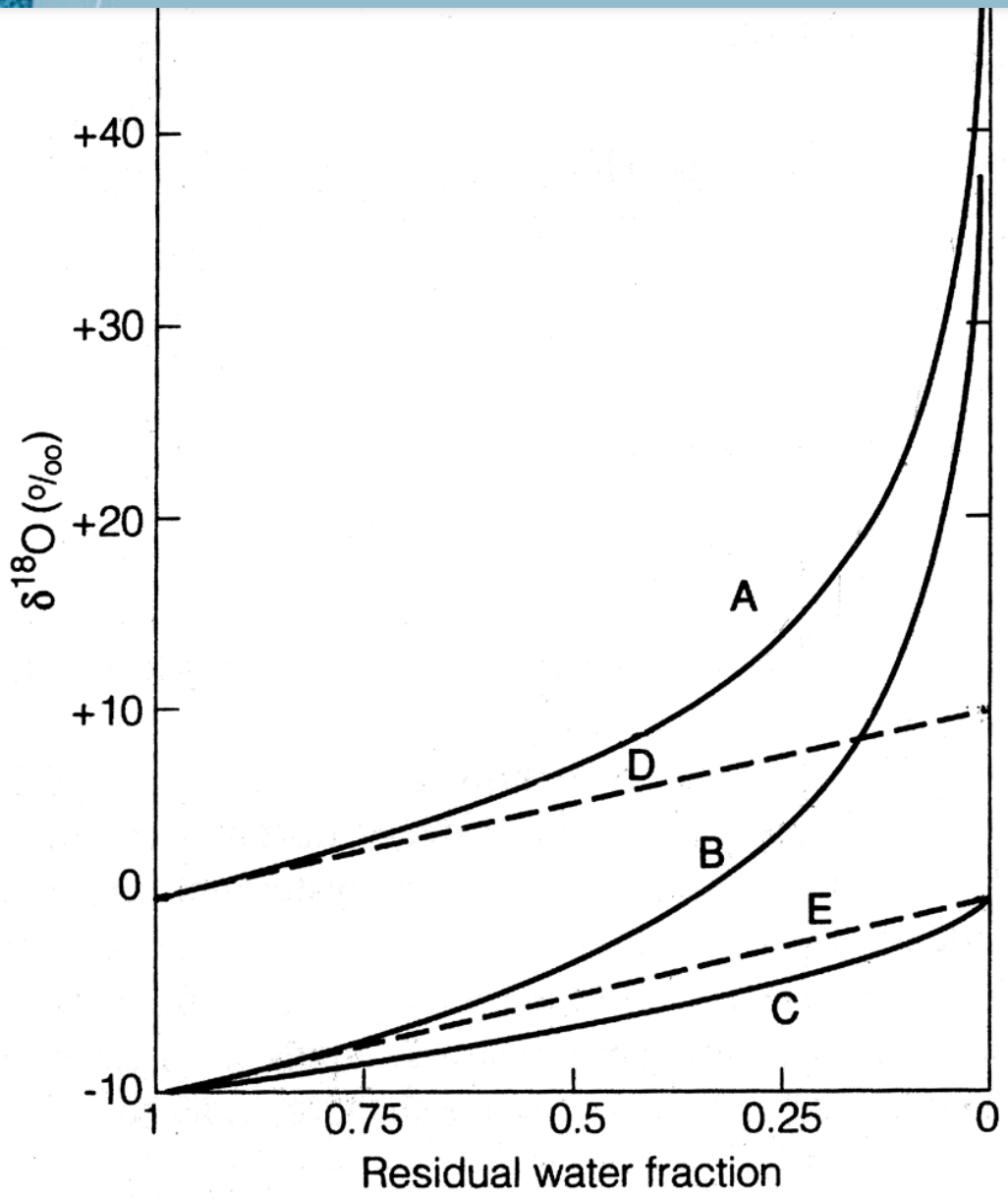
Why does $H_2{}^{16}O$ have a higher vapor pressure?"



- These values are the amount of energy required to break the bond.
- More energy is needed to break the D-D bond than the H-H bond, leading to a lower vapor pressure for D-D bond

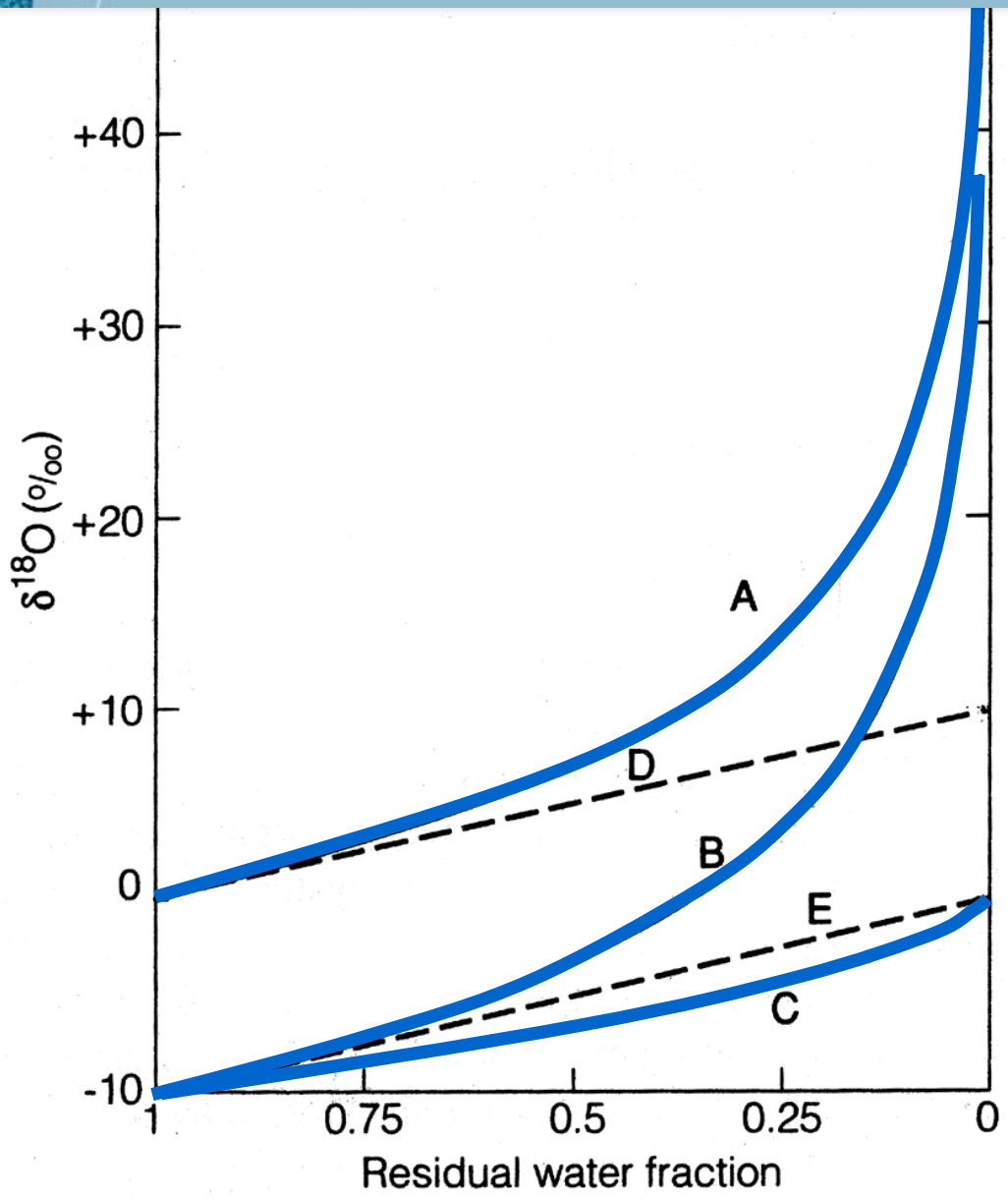
Rayleigh Fractionation

As Rayleigh distillation proceeds, the signatures of both the accumulated vapor mass and the remaining water change. The pattern is dependent on whether you have an "OPEN" or a "CLOSED" system.



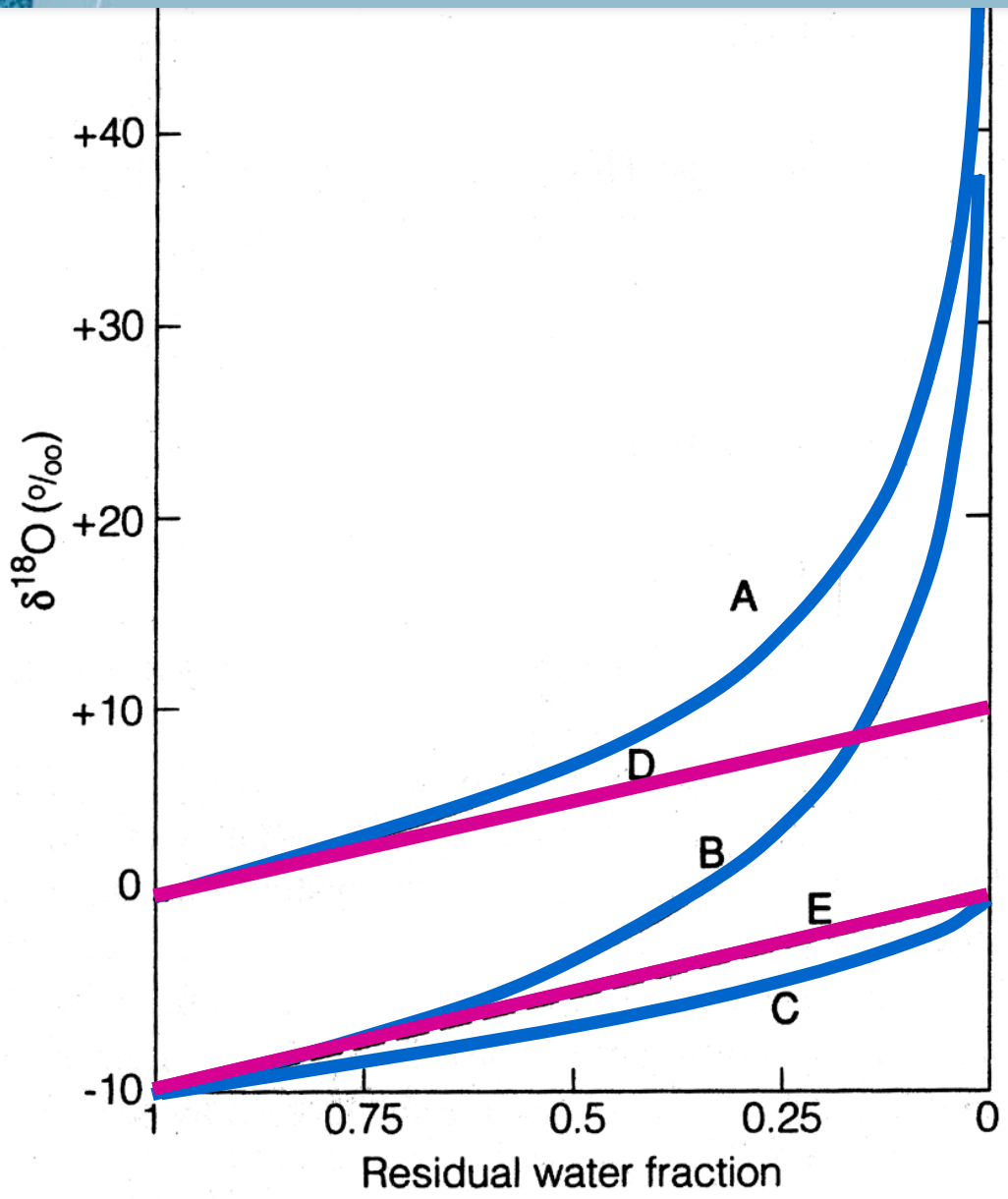
Rayleigh Fractionation

As Rayleigh distillation proceeds, the signatures of both the accumulated vapor mass and the remaining water change. The pattern is dependent on whether you have an "OPEN" or a "CLOSED" system.



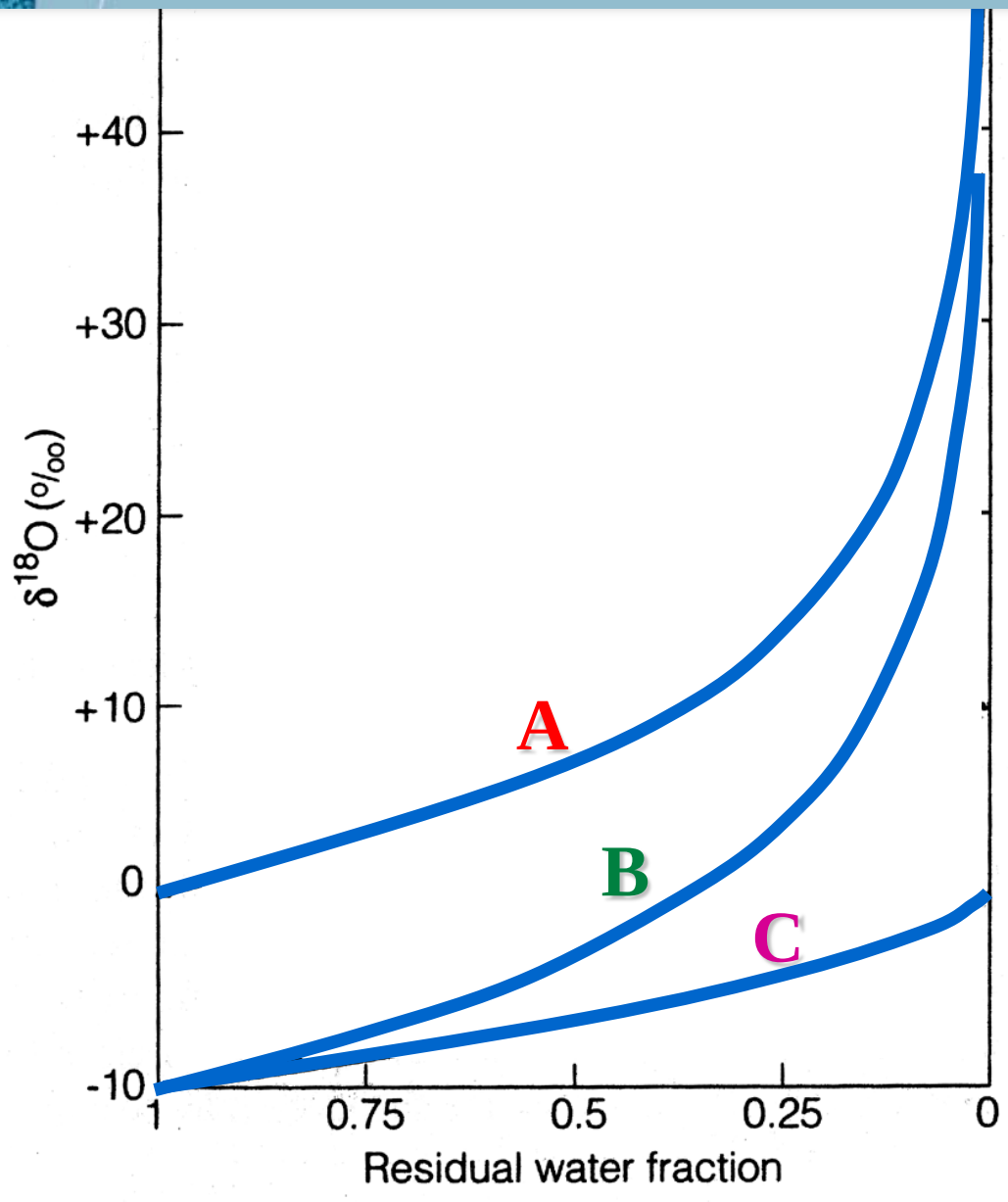
Rayleigh Fractionation

As Rayleigh distillation proceeds, the signatures of both the accumulated vapor mass and the remaining water change. The pattern is dependent on whether you have an "OPEN" or a "CLOSED" system.



Rayleigh Fractionation

In an open system, the vapor is removed as soon as it forms.



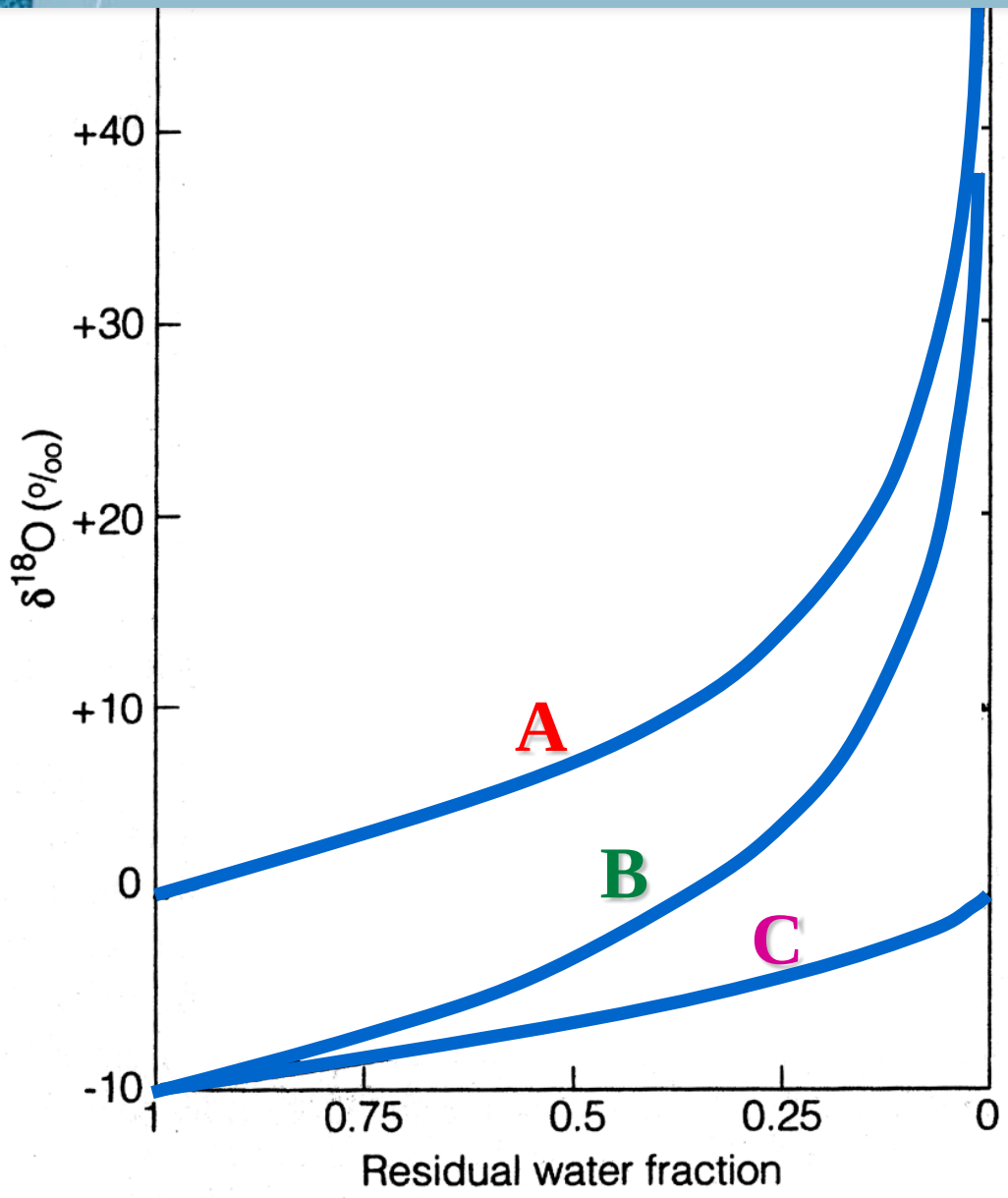
Rayleigh Fractionation

In an open system, the vapor is removed as soon as it forms.

A = remaining water in OPEN system (liquid)

B = instantaneous vapor in OPEN system

C = accumulated vapor fraction being removed from the OPEN system



Rayleigh Fractionation

Consider a systems where a transformation takes place at equilibrium between phase A and B, but then phase B is immediately removed (**open system**).
These equations describe the open system Rayleigh fractionation:

$$R_A = R_{AO} f^{(\alpha-1)}$$

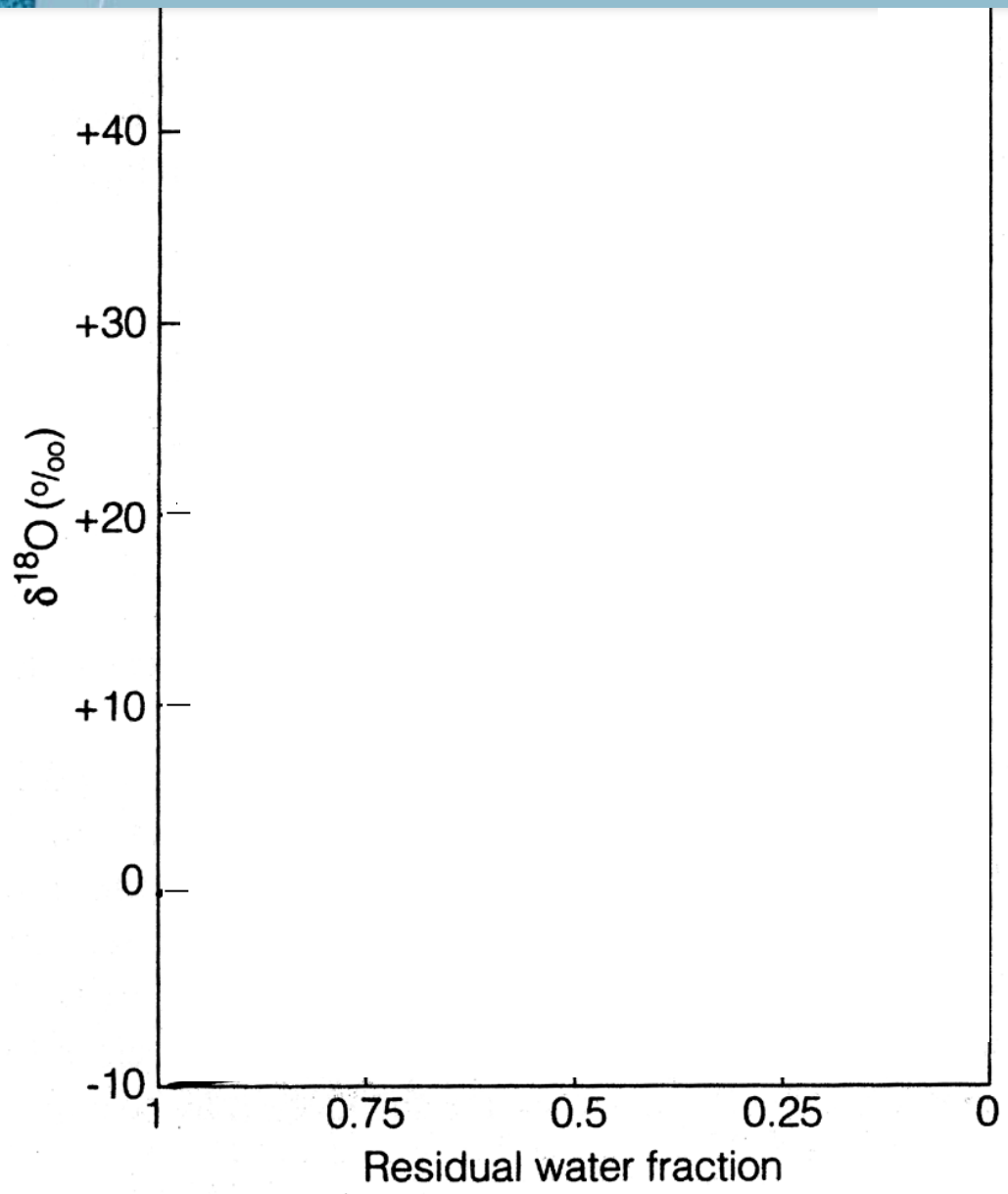
$$R_B = \alpha f^{(\alpha-1)}$$

$$R_C = R_{AO}(1-f^{\alpha})/(1-f)$$

R_A = isotopic of ratio of phase A (**reservoir**) after a certain amount of distillation
R_{AO} = initial isotopic ratio of phase A, f is the fraction of phase A remaining (A/A0 = fraction of phase A remaining), and a is the fractionation factor between phase A and B.
R_B = ratio of the instantaneous product and R_C is the ratio of the accumulated condensate.

Rayleigh Fractionation

In a closed system, the vapor pool is in continuous contact with the liquid pool

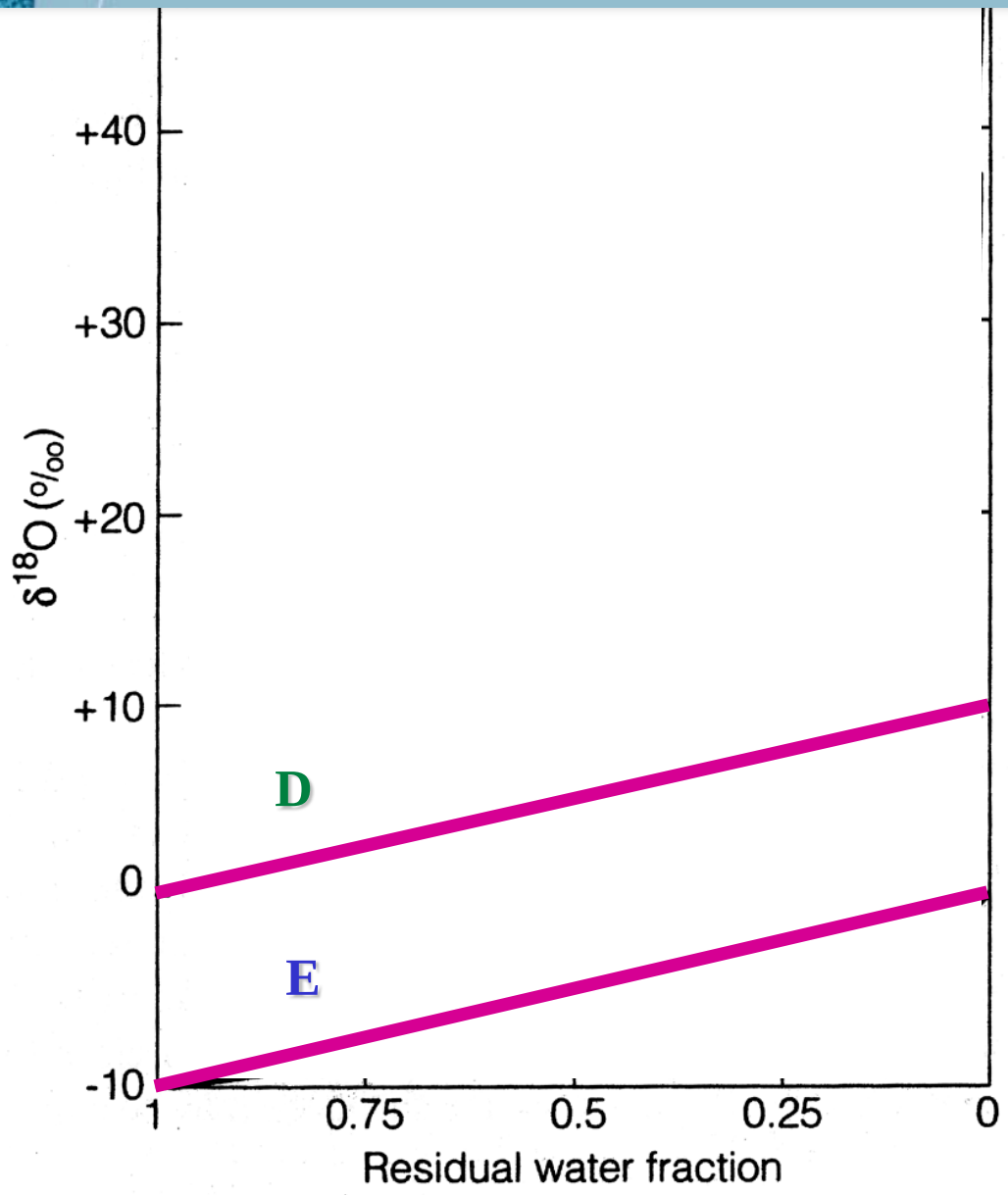


Rayleigh Fractionation

In a closed system, the vapor pool is in continuous contact with the liquid pool

D = $\delta^{18}O$ of water in a CLOSED system

E = $\delta^{18}O$ of vapor in a CLOSED system

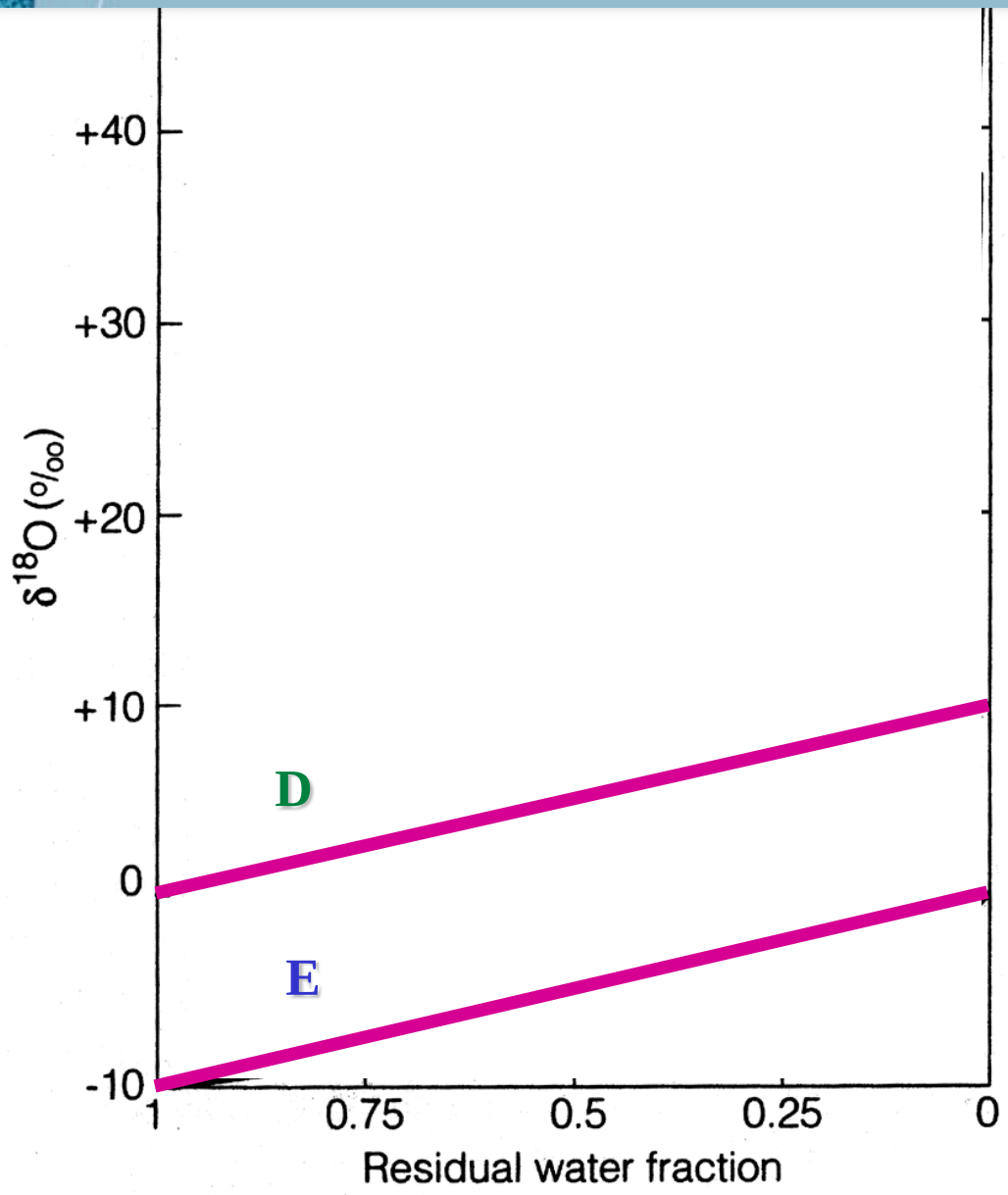


Rayleigh Fractionation

In a closed system, the vapor pool is in continuous contact with the liquid pool

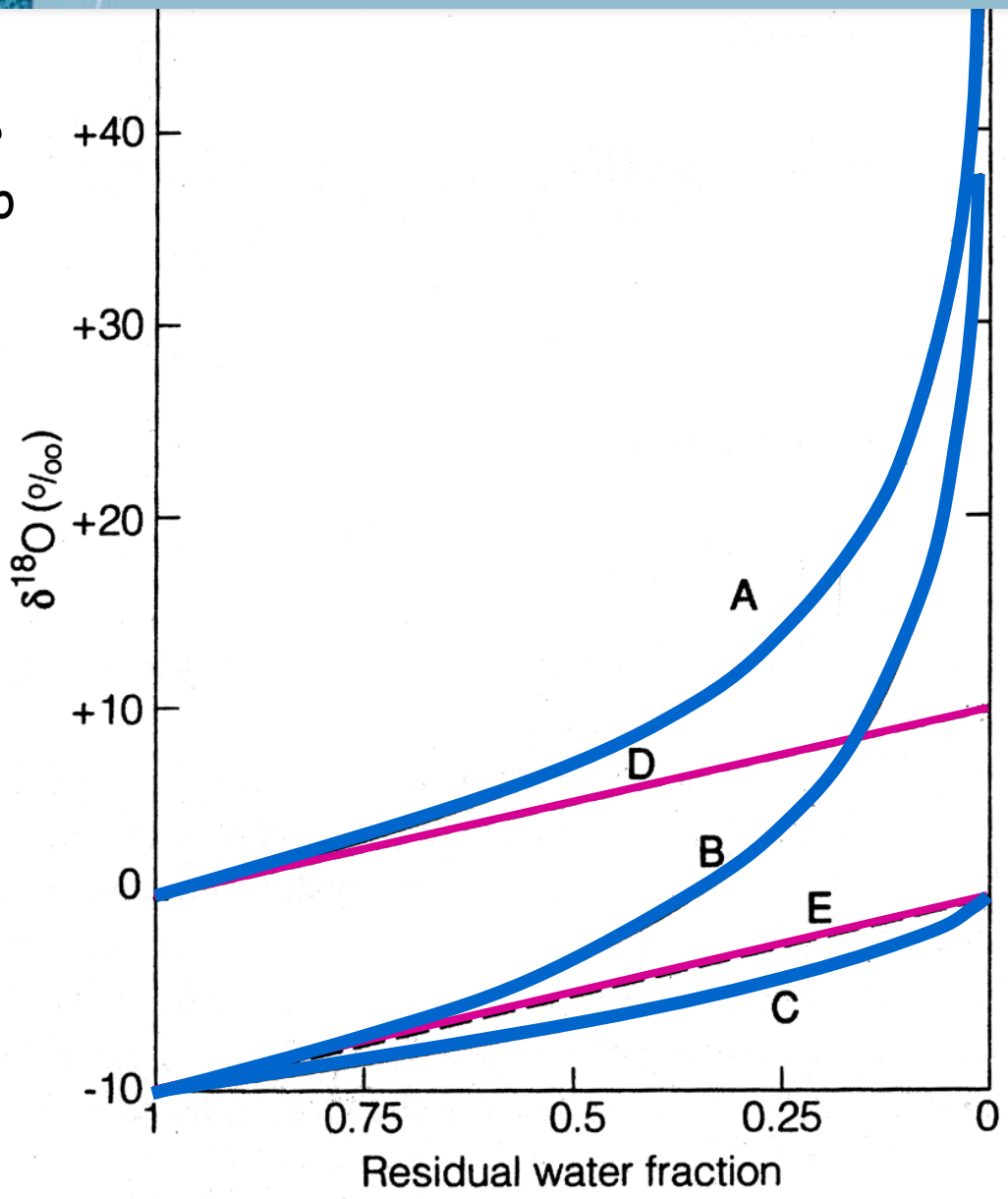
D = $\delta^{18}O$ of water in a CLOSED system

E = $\delta^{18}O$ of vapor in a CLOSED system



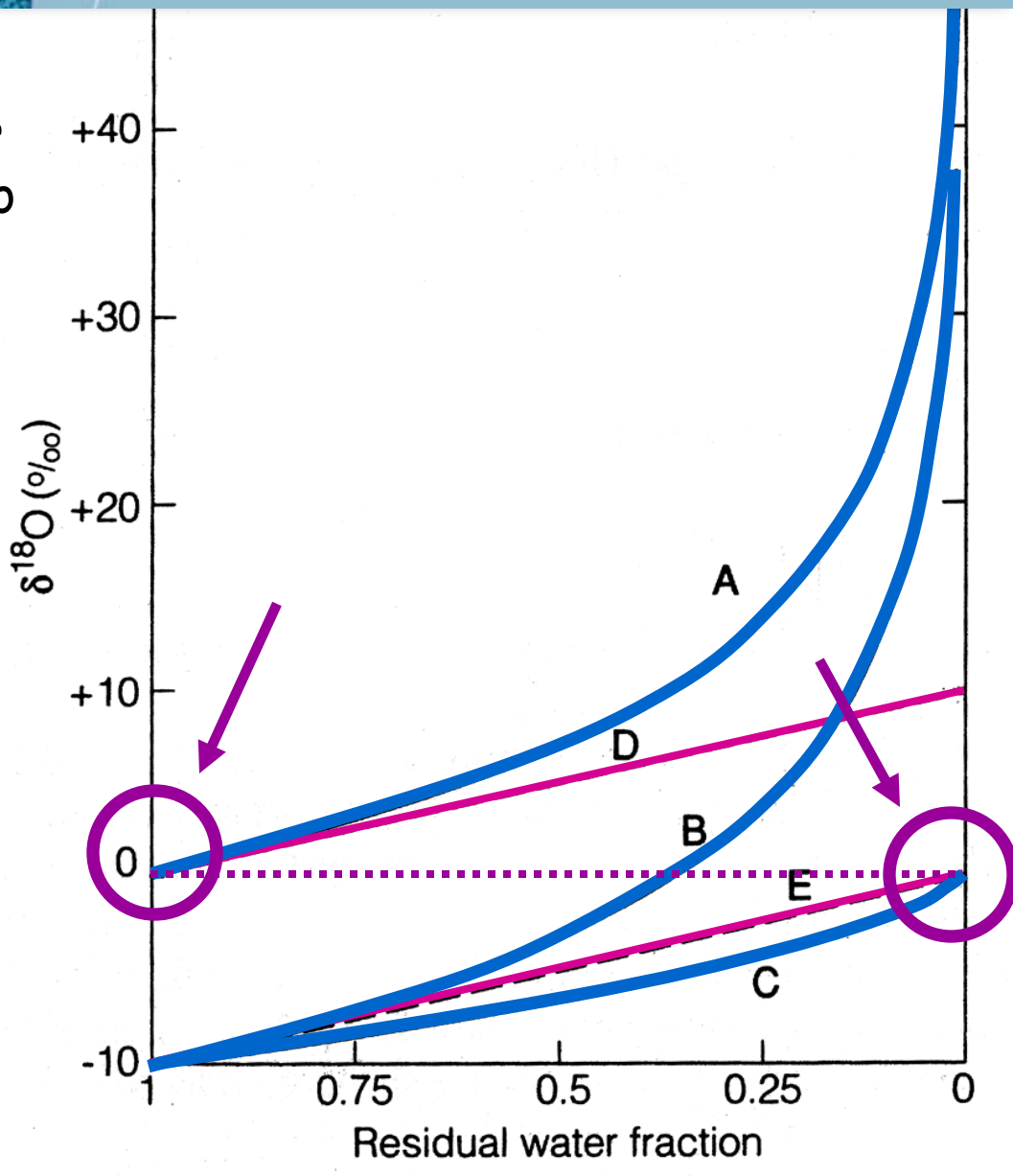
Rayleigh Fractionation

For all systems, if distillation is complete, the accumulated vapor mass must have a δ value equal to the initial water mass



Rayleigh Fractionation

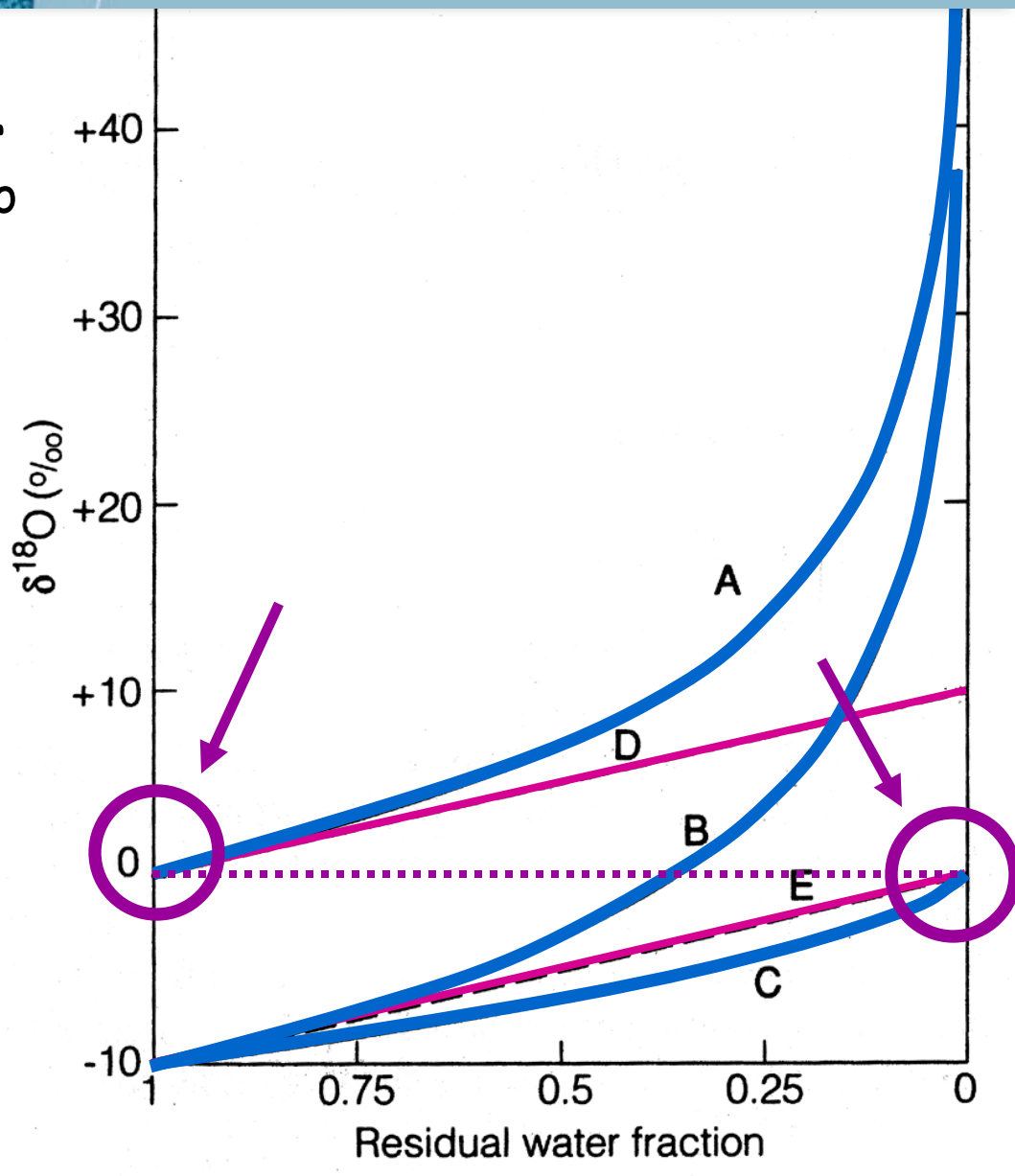
For all systems, if distillation is complete, the accumulated vapor mass must have a δ value equal to the initial water mass



Rayleigh Fractionation

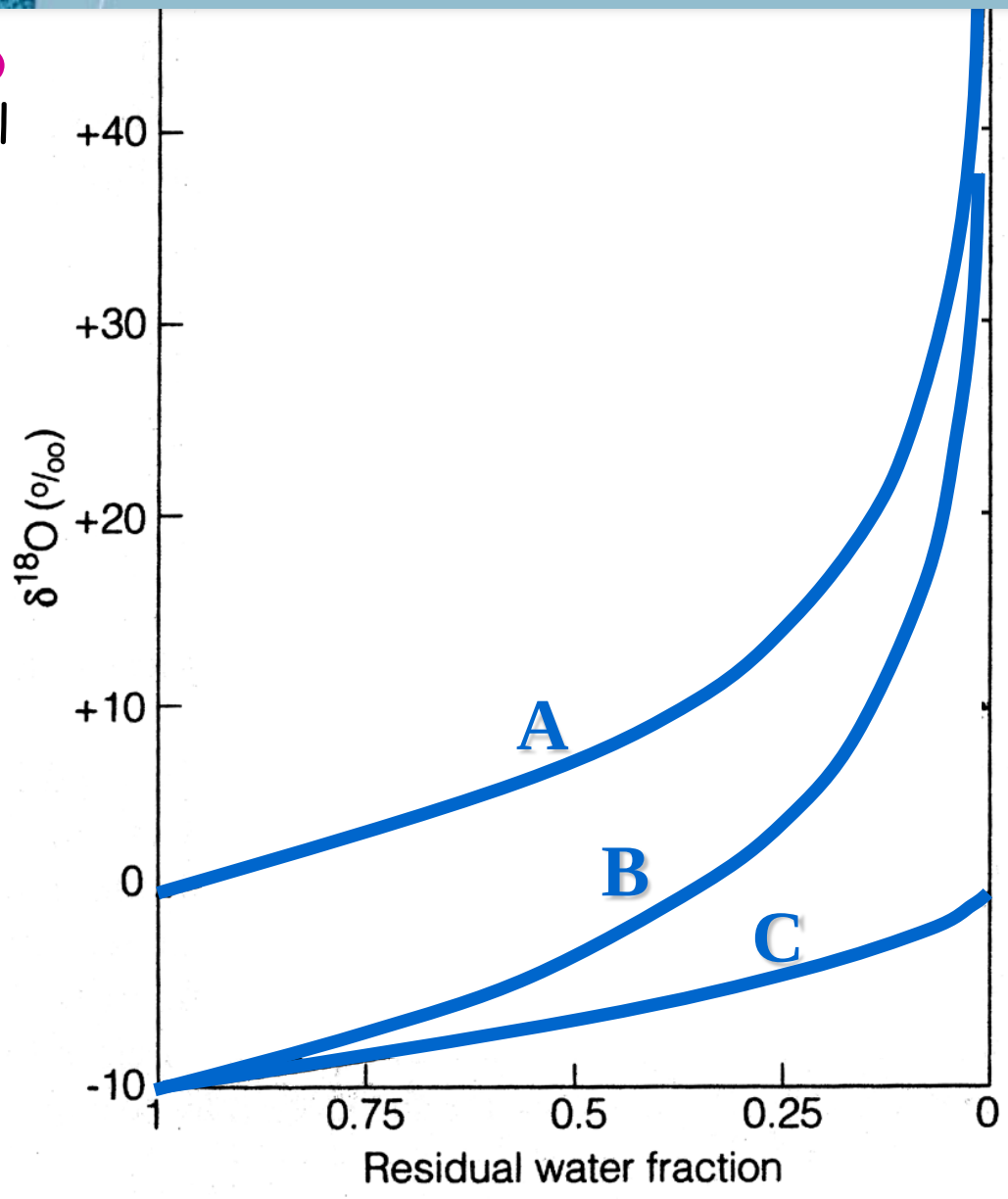
For all systems, if distillation is complete, the accumulated vapor mass must have a δ value equal to the initial water mass

However OPEN vs. CLOSED systems display different instantaneous d offsets between the two pools



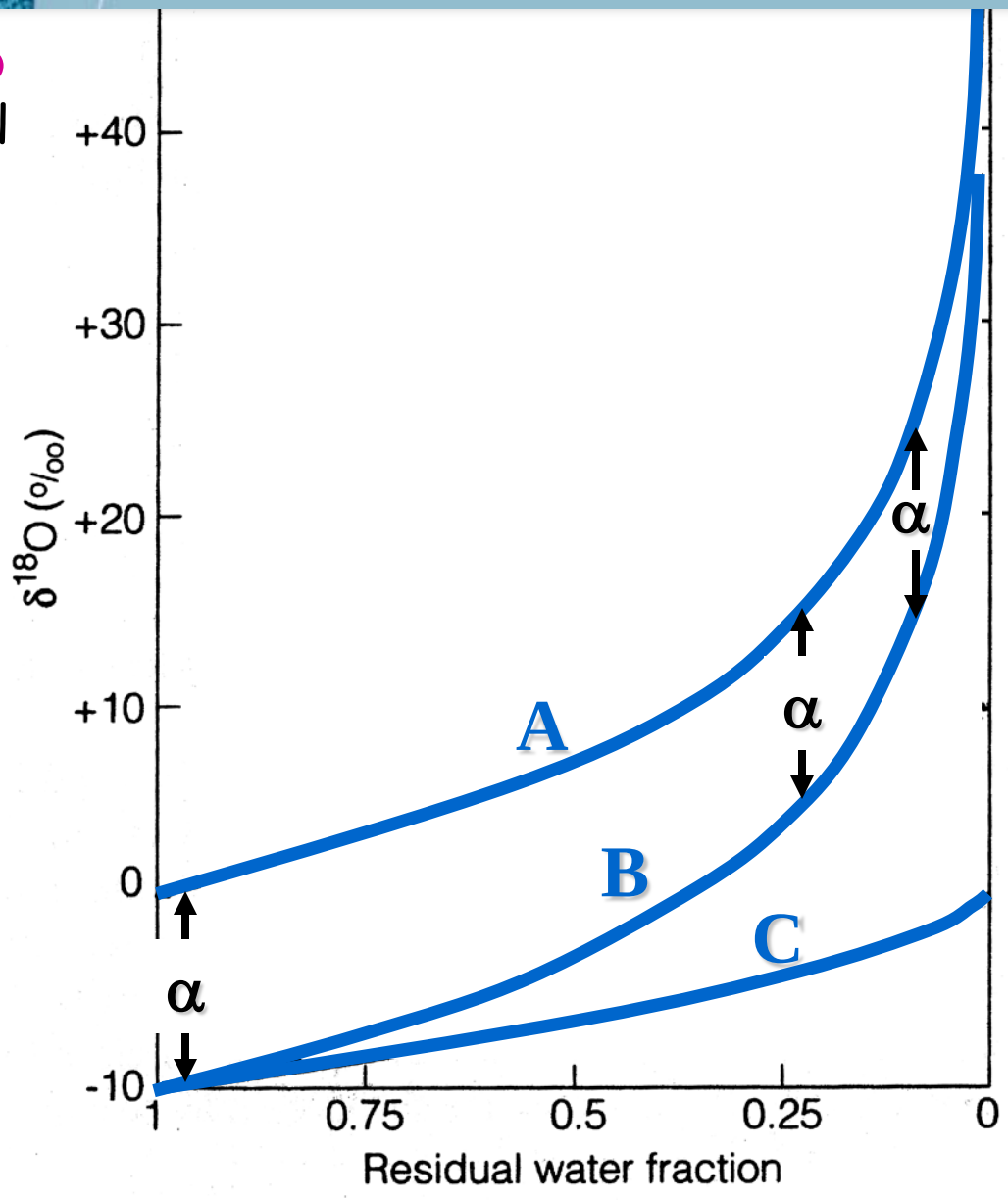
Rayleigh Fractionation

In either an OPEN or a CLOSED system, the remaining liquid pool (A) and instantaneous vapor (B) must be related to one another by the fractionation factor α.



Rayleigh Fractionation

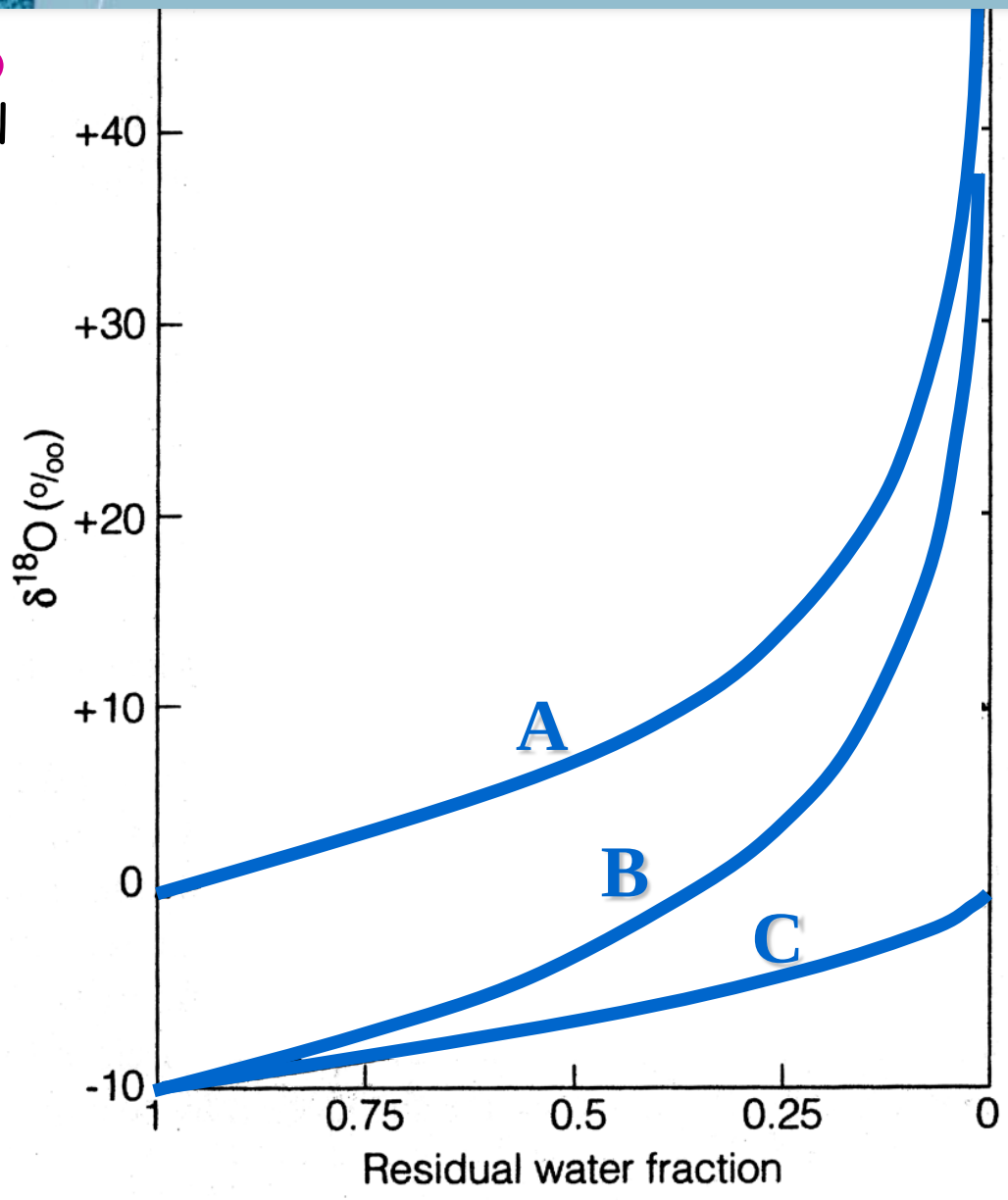
In either an OPEN or a CLOSED system, the remaining liquid pool (A) and instantaneous vapor (B) must be related to one another by the fractionation factor α.



Rayleigh Fractionation

In either an OPEN or a CLOSED system, the remaining liquid pool (A) and instantaneous vapor (B) must be related to one another by the fractionation factor α.

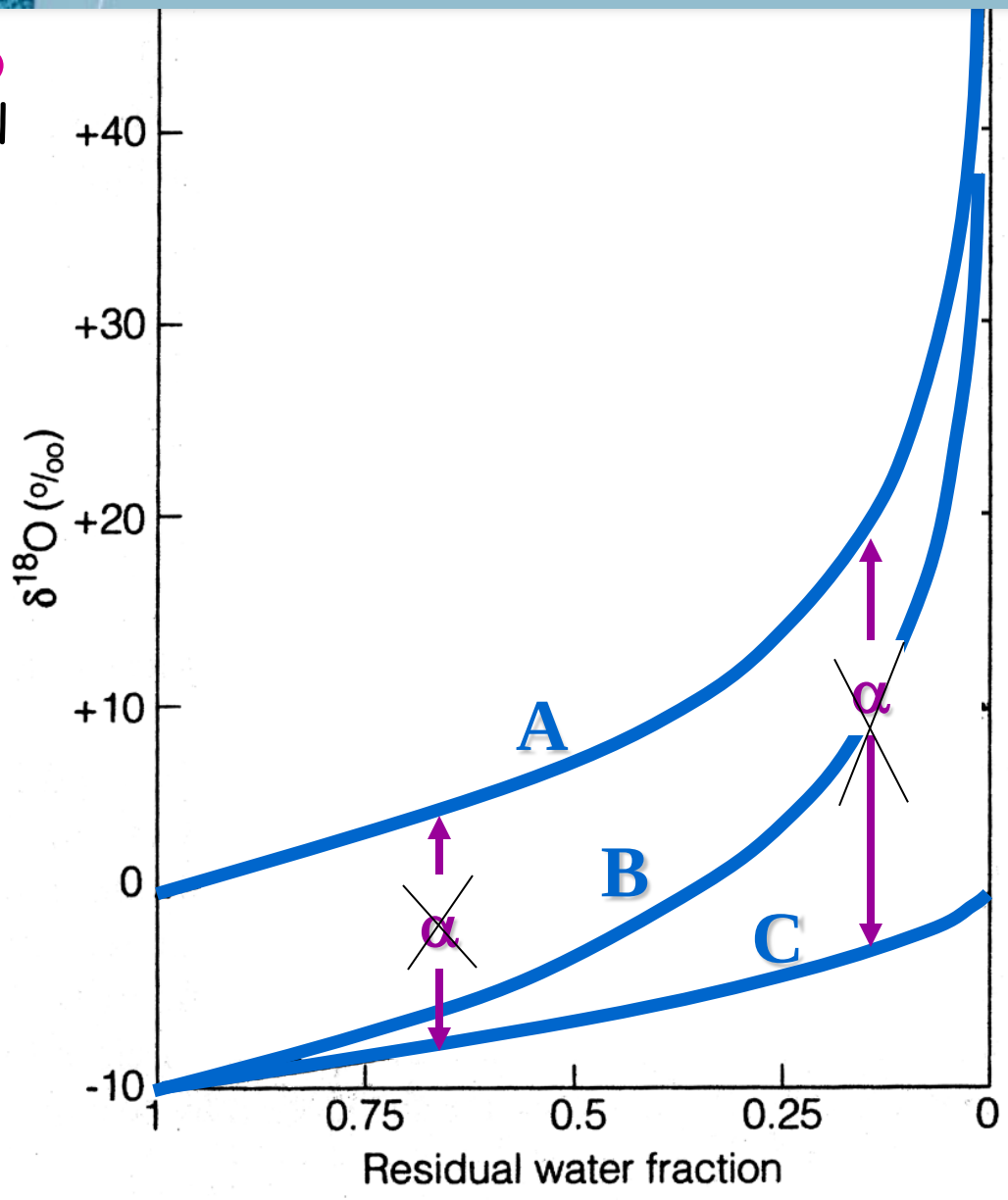
However, in an OPEN system, since the accumulated vapor (C) is not in contact with (A), these two pools are related to one another by α only at the start of the distillation process.



Rayleigh Fractionation

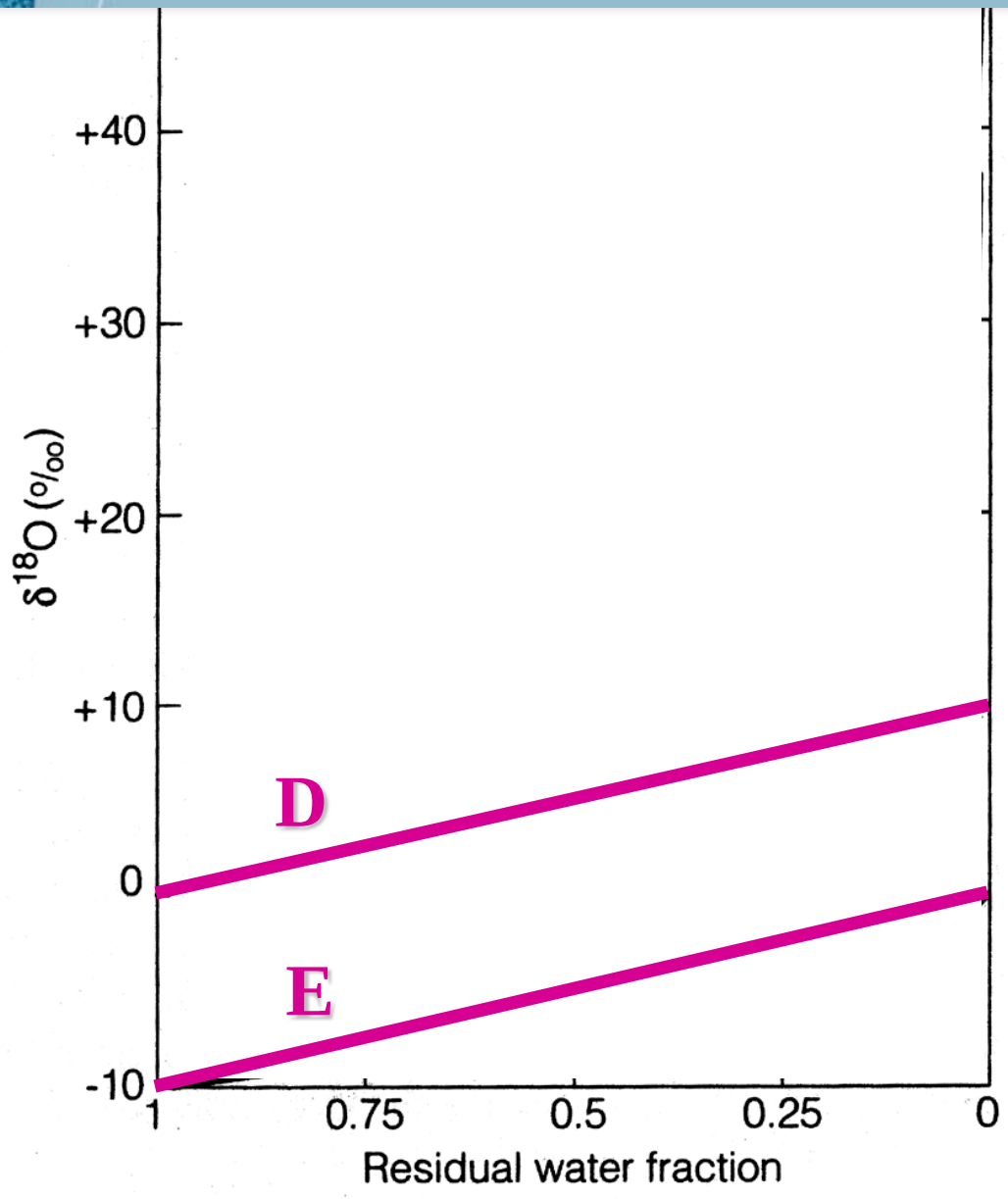
In either an OPEN or a CLOSED system, the remaining liquid pool (A) and instantaneous vapor (B) must be related to one another by the fractionation factor α.

However, in an OPEN system, since the accumulated vapor (C) is not in contact with (A), these two pools are related to one another by α only at the start of the distillation process.



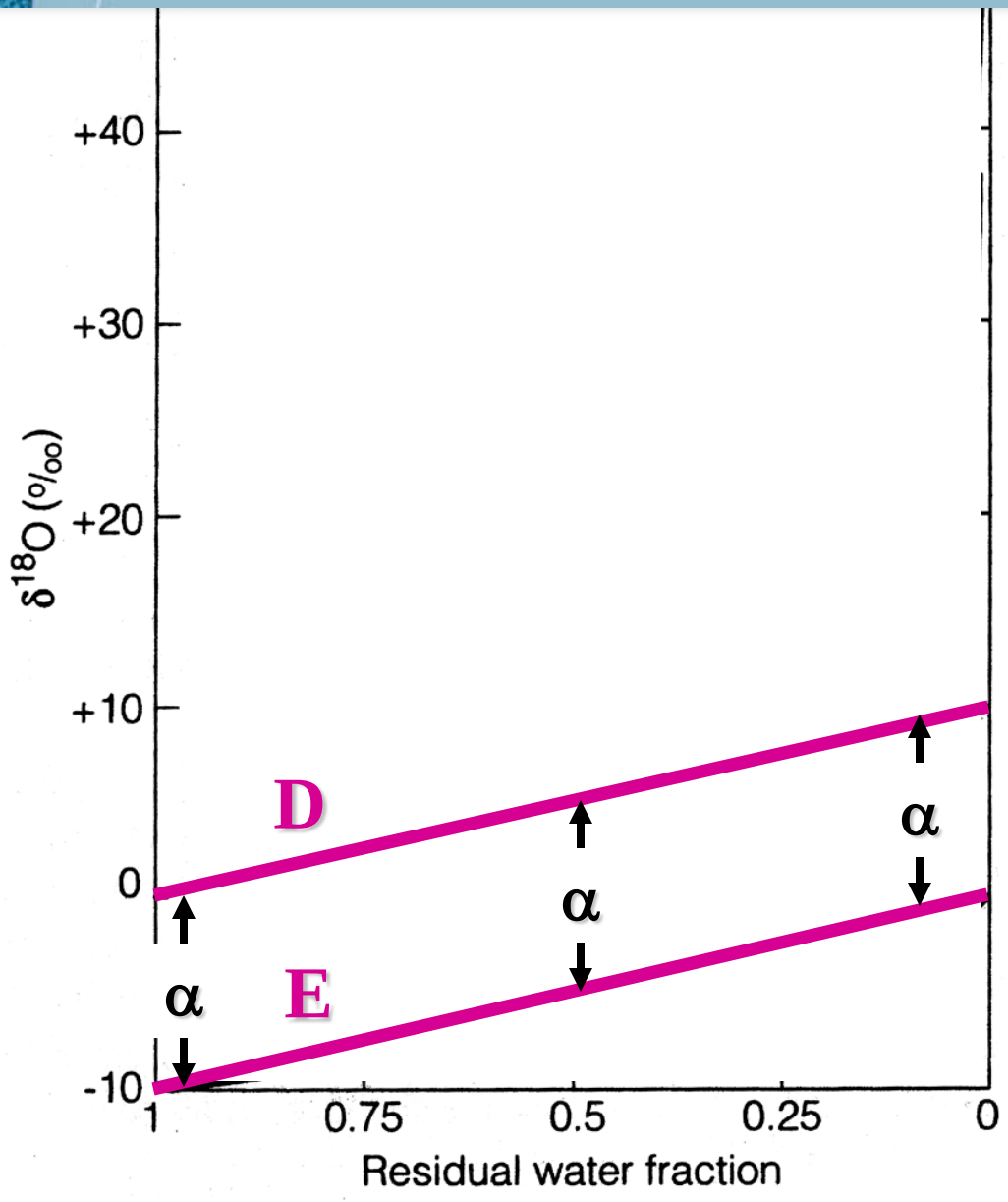
Rayleigh Fractionation

In a CLOSED system the two pools never differ by more than α because as distillation proceeds, the isotopes in the two pools will always equilibrate with one another.



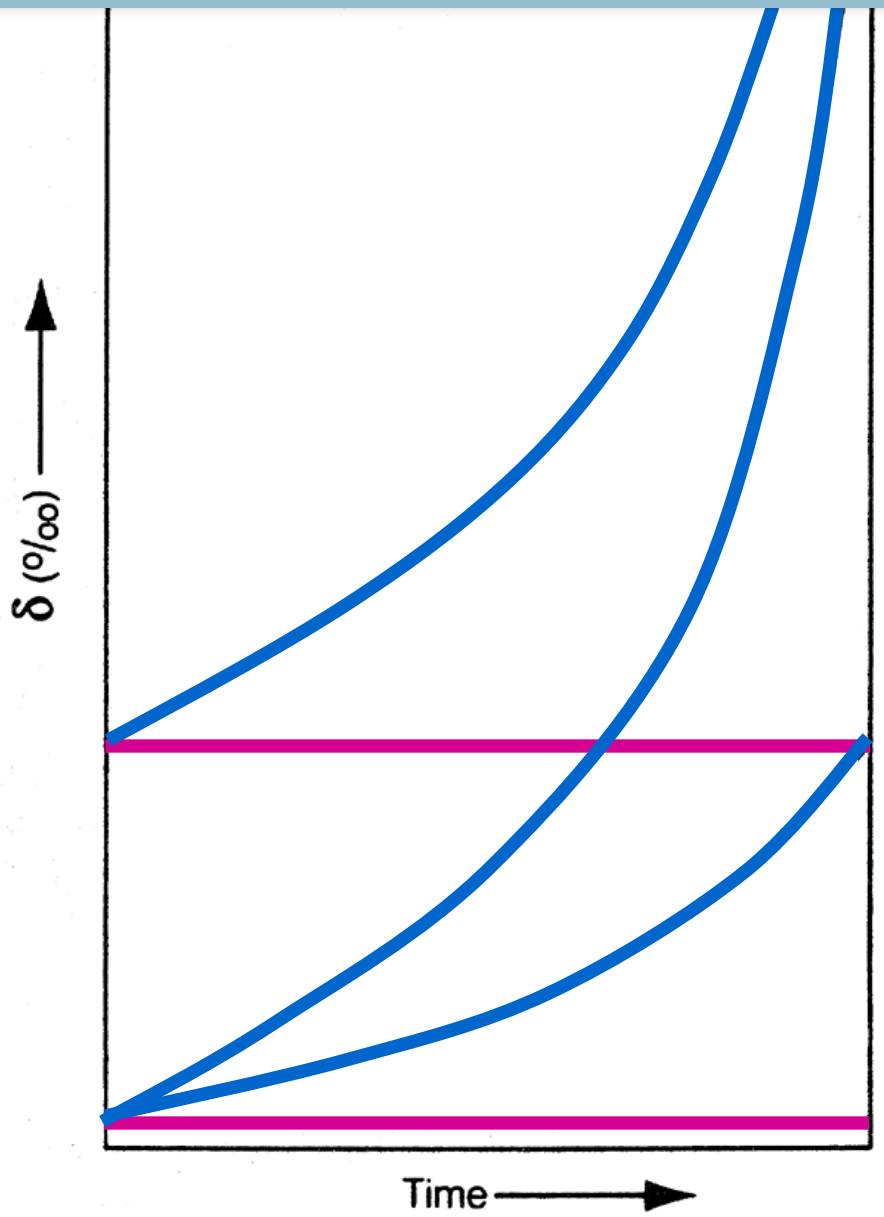
Rayleigh Fractionation

In a CLOSED system the two pools never differ by more than α because as distillation proceeds, the isotopes in the two pools will always equilibrate with one another.



Rayleigh Fractionation

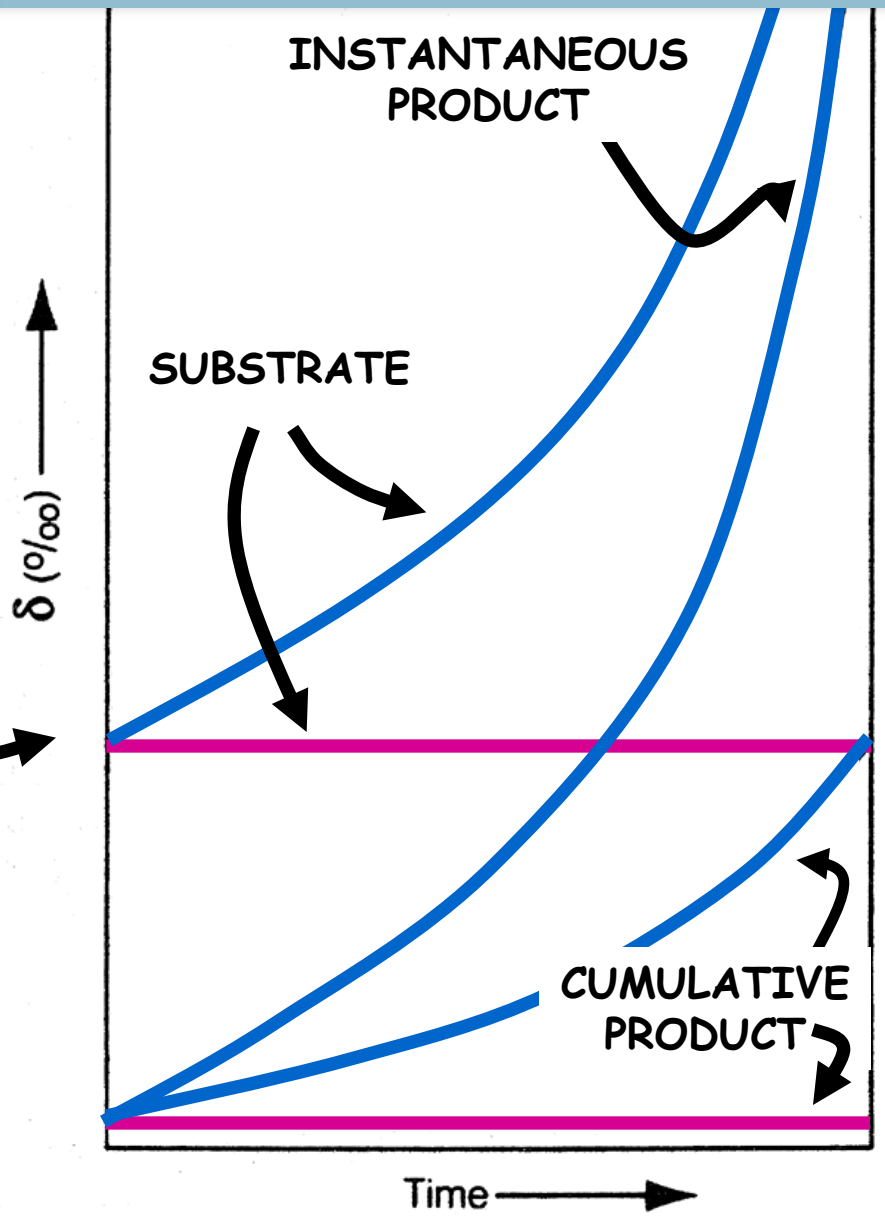
Rayleigh distillation is an equilibrium process. However, similar rules apply to UNI-DIRECTIONAL REACTIONS.



Rayleigh Fractionation

Rayleigh distillation is an equilibrium process. However, similar rules apply to UNI-DIRECTIONAL REACTIONS.

ONCE AGAIN

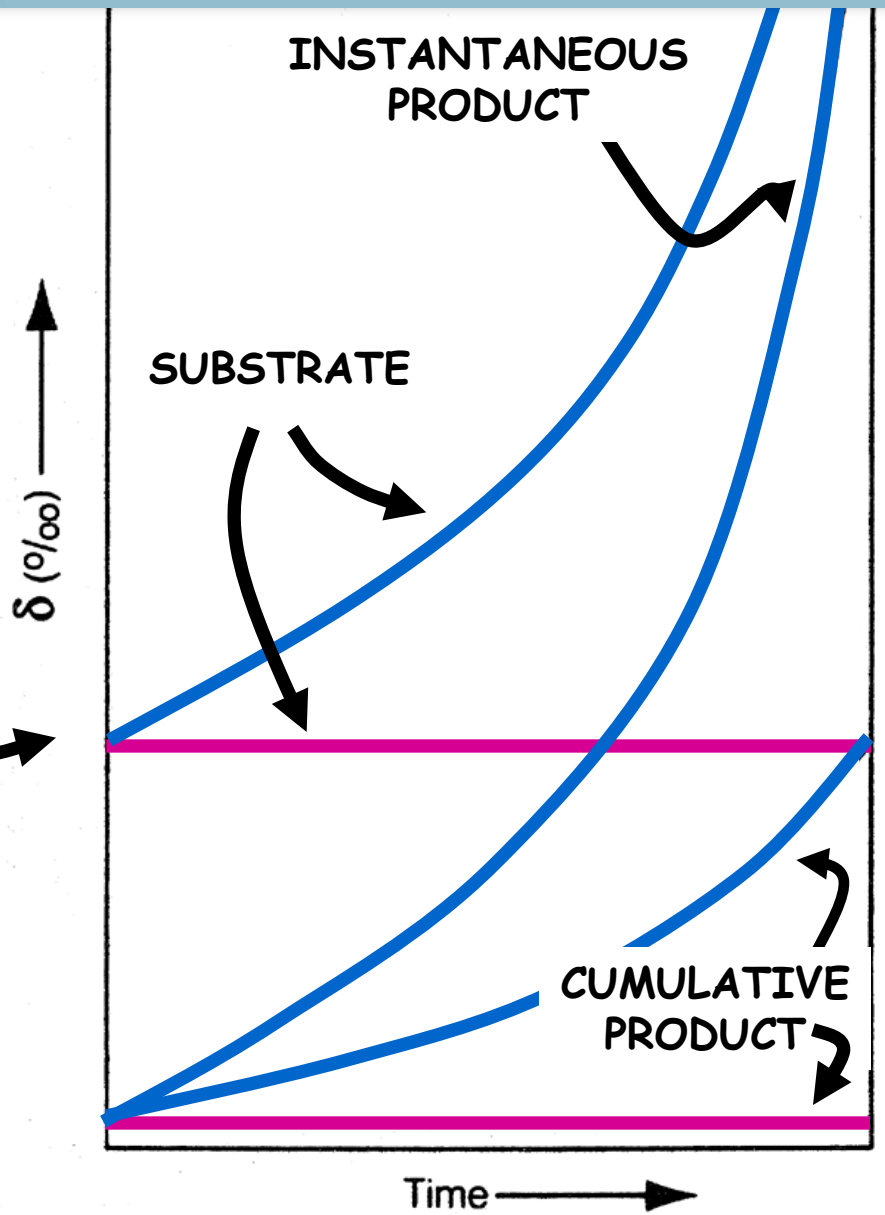


Rayleigh Fractionation

Rayleigh distillation is an equilibrium process. However, similar rules apply to UNI-DIRECTIONAL REACTIONS.

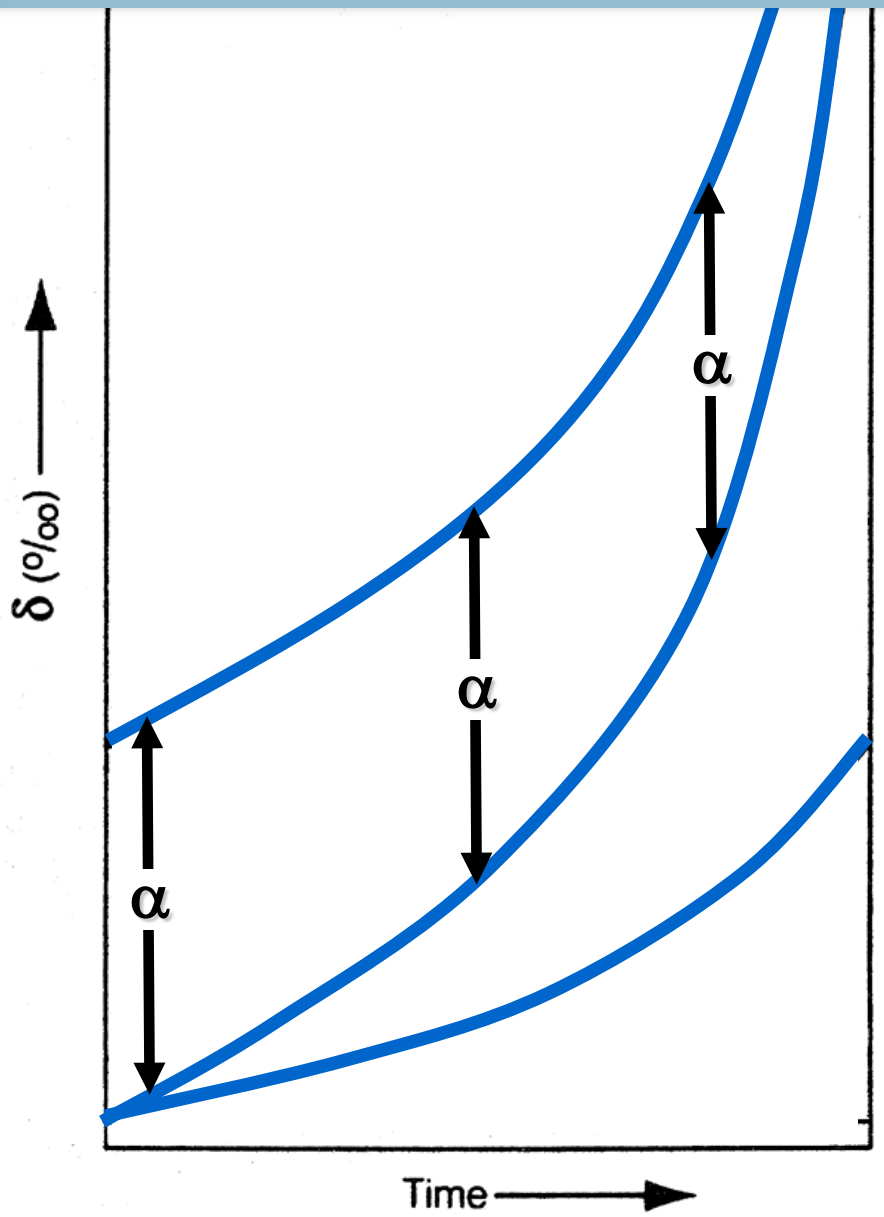
ONCE AGAIN

With uni-directional reactions the important distinction is between FINITE and INFINITE amounts of substrate



Rayleigh Fractionation

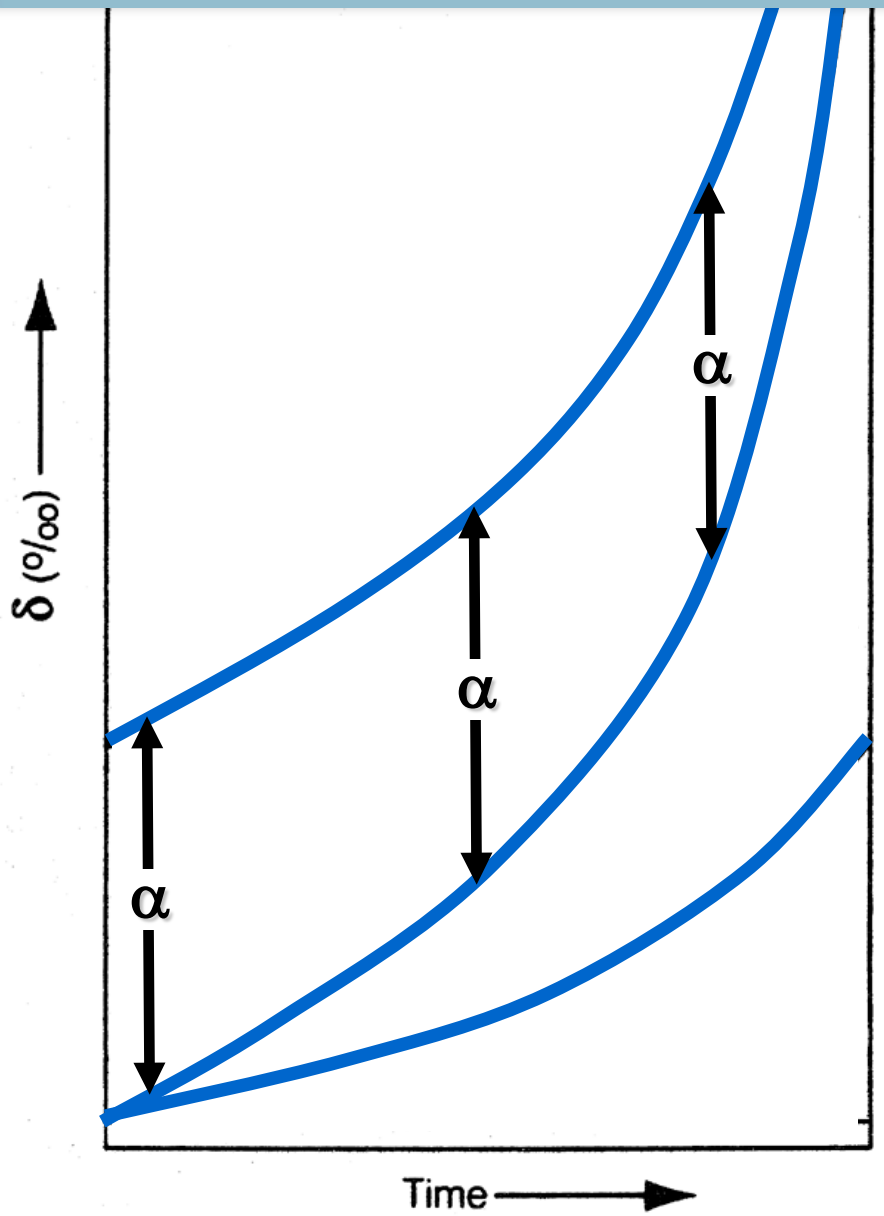
If FINITE amounts of substrate exist, the creation of product noticeably changes the δ value of the remaining substrate



Rayleigh Fractionation

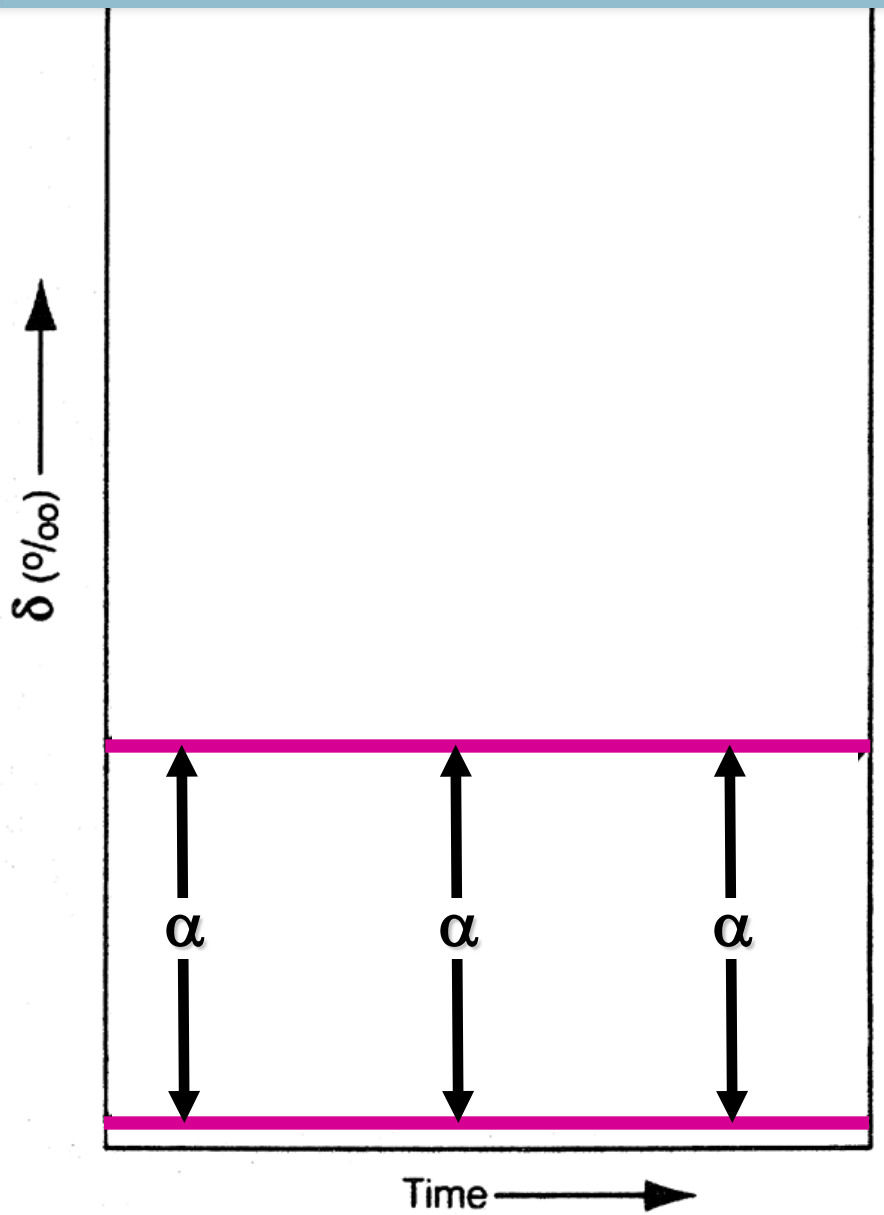
If FINITE amounts of substrate exist, the creation of product noticeably changes the δ value of the remaining substrate

Therefore, the value of both the substrate and the instantaneous product will change over time, although they will always be related to one another by the fractionation factor α



Rayleigh Fractionation

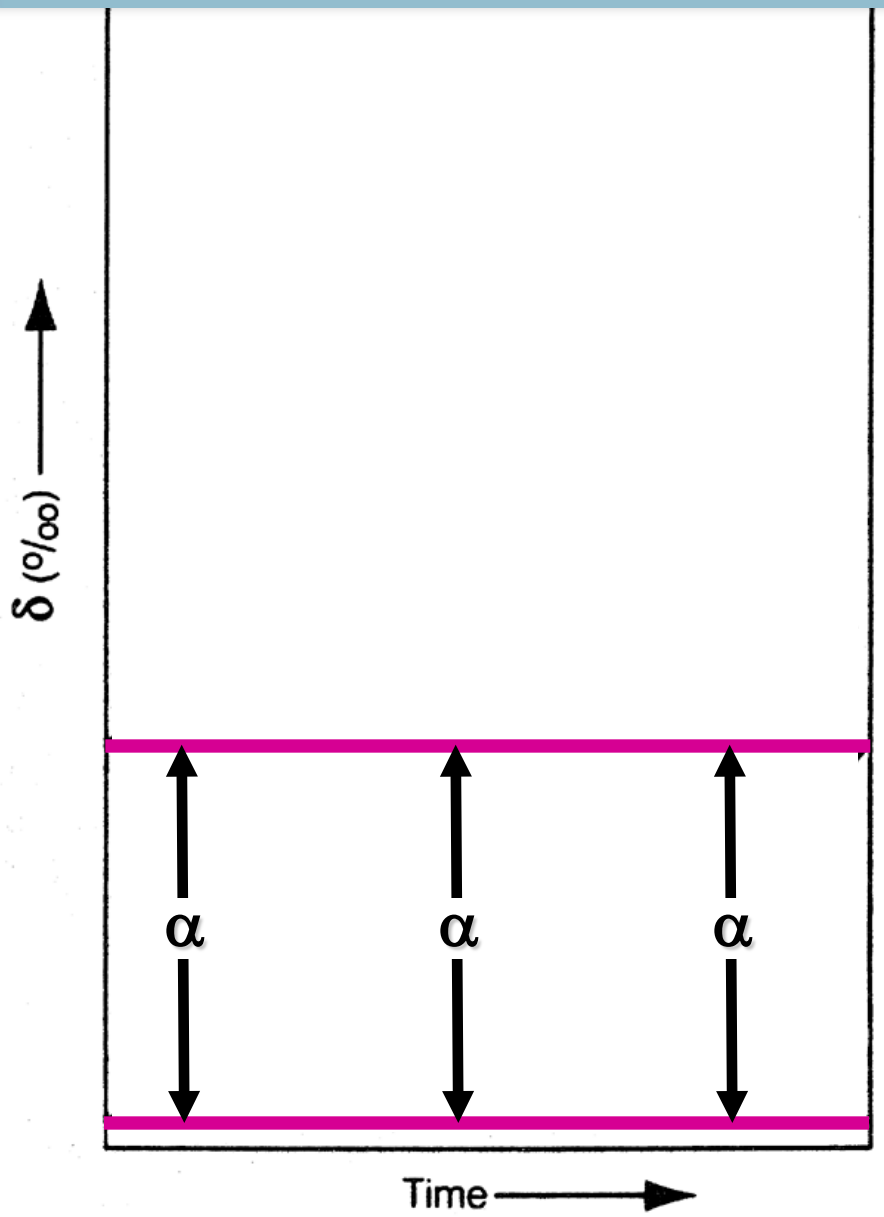
If INFINITE amounts of substrate exist, the conversion of substrate to product does not noticeably change the δ value of the remaining substrate



Rayleigh Fractionation

If INFINITE amounts of substrate exist, the conversion of substrate to product does not noticeably change the δ value of the remaining substrate

Therefore the δ values of the substrate and product remain constant over time and are always related by the fractionation factor α



This project has received funding from the
European Union's Horizon 2020 research and innovation
programme under grant agreement No 643084