



[Equilibrium partitioning of organic compounds](#)

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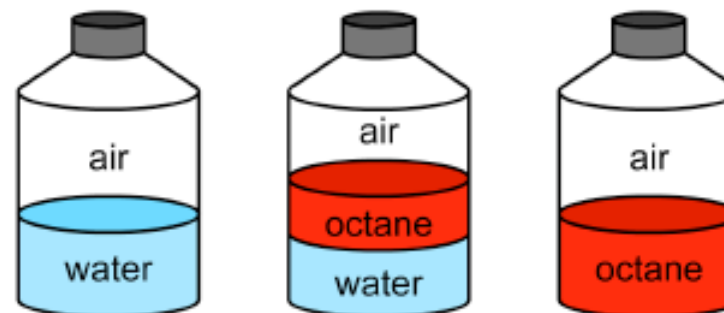
Equilibrium partitioning between different phases

In the following exercise, the equilibrium partitioning of water and organic compounds has to be appraised in two and three phase systems.

Click on   to navigate through the exercises,
Fill in , and check your answers by pressing !

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next



Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

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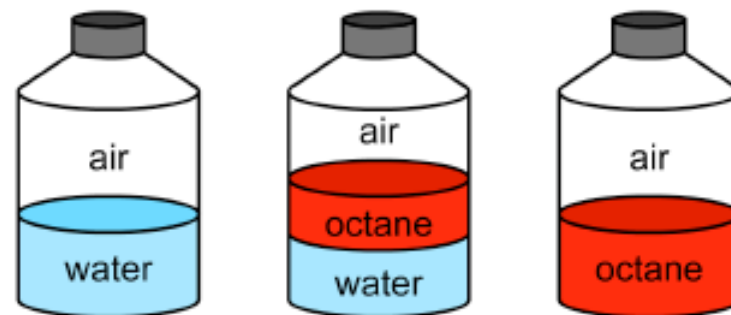
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Equilibrium partitioning between different phases

Note:

c_{i1}^* denotes the **equilibrium** concentration of i in phase 1, while c_{i1}^0 denotes the **initial** concentration of i in phase 1. That is, this is the concentration before this phase gets into contact with other phases of the system (i.e., before initiation of the partitioning process).

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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a) Equilibrium partitioning of water

between different phases

Info: Below, you see the equilibrium partitioning of water into the gas phase at 25°C.



$$^*C_{H_2O} = 0.0013 \text{ mol/L} = 3169 \text{ Pa}$$

$$^*C_{H_2O} = 55 \text{ mol/L}$$

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

Equilibrium partitioning of organic compounds

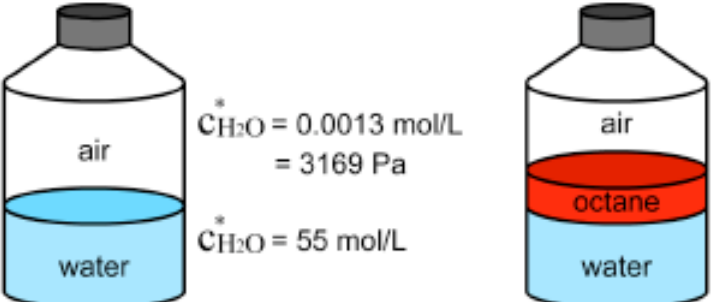
Question 15

▶ [Some fundamentals ...](#)▶ [Summary and further information](#)▶ [Self test](#)▼ [Problems](#)↓ [Question 1](#)↓ [Answer](#)↓ [Question 2](#)↓ [Answer](#)↓ [Question 3](#)↓ [Answer](#)↓ [Question 4](#)↓ [Answer](#)↓ [Question 5](#)↓ [Answer](#)↓ [Question 6](#)↓ [Answer](#)↓ [Question 7](#)↓ [Answer](#)↓ [Question 8](#)↓ [Answer](#)↓ [Question 9](#)↓ [Answer](#)↓ [Question 10](#)↓ [Answer](#)↓ [Question 11](#)↓ [Answer](#)↓ [Question 12](#)↓ [Answer](#)↓ [Question 13](#)↓ [Answer](#)↓ [Question 14](#)↓ [Answer](#)↓ **Question 15**↓ [Question 16](#)↓ [Question 17](#)**a) Equilibrium partitioning of water****between different phases**

What can you say about the equilibrium concentrations of water in the gas phase if the pure water phase is covered by a very hydrophobic organic liquid (e.g., octane) that, in equilibrium with the pure water phase, contains only a very tiny amount of water molecules?

Enter your guess into the input text fields and press CHECK!

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Left bottle (air over water):

- air: $C_{\text{H}_2\text{O}}^* = 0.0013 \text{ mol/L}$
 $= 3169 \text{ Pa}$
- water: $C_{\text{H}_2\text{O}}^* = 55 \text{ mol/L}$

Right bottle (air over octane over water):

- air: $C_{\text{H}_2\text{O}}^* =$ mol/L
 $=$ Pa
- octane: $C_{\text{H}_2\text{O}}^* = 0.0024 \text{ mol/L}$
- water: $C_{\text{H}_2\text{O}}^* = 55 \text{ mol/L}$

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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a) Equilibrium partitioning of water

between different phases

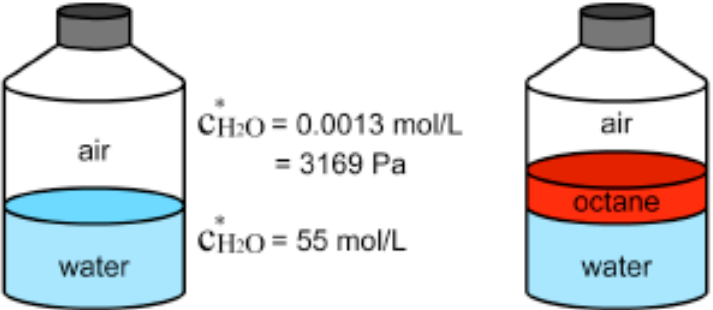
No, unfortunately you are wrong ...

Read carefully through the solution below, and try again!

Solution

The equilibrium concentration of water vapour in the gas phase above the octane should be the same as it would be above the pure water phase. This is due to the fact that the tendency of water to partition out of its own pure phase into the gas phase only depends on the interactions that it has in its own pure phase and on the temperature of the system (by virtue of the thermal energy distribution of water molecules).

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Left bottle (air over water):

- air: $C_{\text{H}_2\text{O}}^* = 0.0013 \text{ mol/L}$
- water: $C_{\text{H}_2\text{O}}^* = 55 \text{ mol/L}$
- Pressure: $= 3169 \text{ Pa}$

Right bottle (air over octane over water):

- air: $C_{\text{H}_2\text{O}}^* = \text{[input box]} \text{ mol/L}$
- octane: $C_{\text{H}_2\text{O}}^* = 0.0024 \text{ mol/L}$
- water: $C_{\text{H}_2\text{O}}^* = 55 \text{ mol/L}$
- Pressure: $= \text{[input box]} \text{ Pa}$

CHECK

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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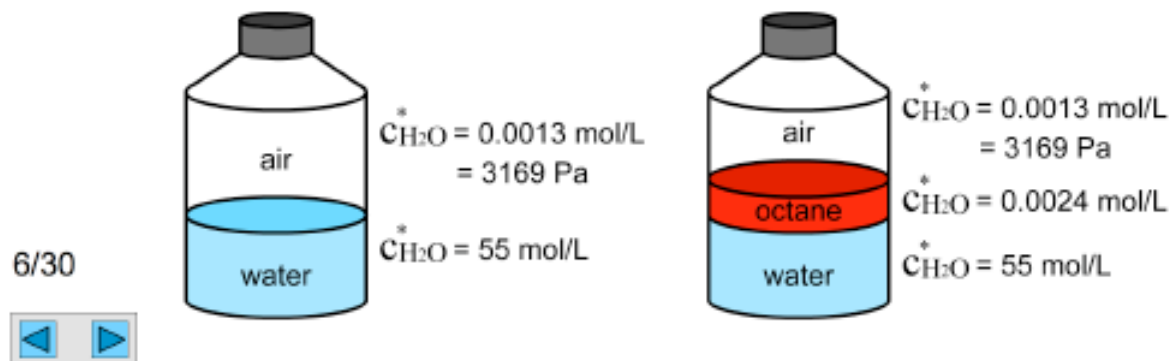
a) Equilibrium partitioning of water

between different phases

Solution

The equilibrium concentration of water vapour in the gas phase above the octane should be the same as it would be above the pure water phase. This is due to the fact that the tendency of water to partition out of its own pure phase into the gas phase only depends on the interactions that it has in its own pure phase and on the temperature of the system (by virtue of the thermal energy distribution of water molecules).

But does this line of argument still hold here because one may raise the point that the water molecules from the water phase have no direct access to the gas phase?



Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

[Equilibrium partitioning of organic compounds](#)

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a) Equilibrium partitioning of water between different phases

Solution

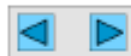
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But does this line of argument still hold here because one may raise the point that the water molecules from the water phase have no direct access to the gas phase?

The answer is **YES**, the line of argument is valid. Of course the water molecules first have to partition into the octane phase and then from octane into the gas phase. However, recall that if water and octane are in equilibrium, then the tendency to escape both phases must be the same. And that means that the equilibrium water concentration in the gas phase is the same above water saturated octane as it is above pure liquid water.

Try the virtual experiment (link below)!

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

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a) Equilibrium partitioning of water between different phases

Solution

Hence, in thermodynamic terms, the presence of octane has no effect on the equilibrium situation. However, the presence of octane greatly affects the kinetics of the system: the time required to reach equilibrium (i.e., the time to move the required amount of water molecules from water to the gas phase) will be much longer in the presence of octane. This is due to the fact that the octane phase cannot hold much water at any point of time, so that the diffusive flux of water molecules via the octane film is much smaller than the direct diffusive flux across the water-air interface.

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

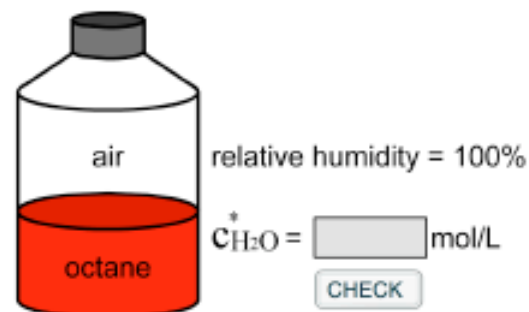
[Equilibrium partitioning of organic compounds](#)

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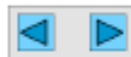
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b) Equilibrium between different phases (25°C)

What is the equilibrium concentration of water in octane in the following system?



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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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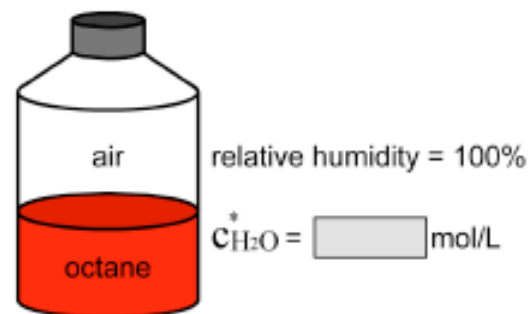
[Some fundamentals ...](#)[Summary and further information](#)[Self test](#)[Problems](#)[Question 1](#)[Answer](#)[Question 2](#)[Answer](#)[Question 3](#)[Answer](#)[Question 4](#)[Answer](#)[Question 5](#)[Answer](#)[Question 6](#)[Answer](#)[Question 7](#)[Answer](#)[Question 8](#)[Answer](#)[Question 9](#)[Answer](#)[Question 10](#)[Answer](#)[Question 11](#)[Answer](#)[Question 12](#)[Answer](#)[Question 13](#)[Answer](#)[Question 14](#)[Answer](#)[Question 15](#)[Question 16](#)[Question 17](#)

b) Equilibrium between different phases (25°C)

Solution

This question is tricky because the information provided in the figure is somewhat ambiguous. The concentration of water in octane in equilibrium with a water saturated gas phase (100% rh) is of course the same as presented in the previous figure.

This situation may experimentally be established in an open system by passing water-saturated gas over the octane phase until attainment of equilibrium. At which point, of course, the lid could be closed without any net changes occurring thereafter.



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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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b) Equilibrium between different phases (25°C)

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This situation may experimentally be established in an open system by passing water-saturated gas over the octane phase until attainment of equilibrium. At which point, of course, the lid could be closed without any net changes occurring thereafter.

Would it be possible to obtain the same situation if we started out with a pure octane phase and added a saturated gas phase and closed the system?

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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b) Equilibrium between different phases (25°C)

Solution

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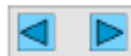
This situation may experimentally be established in an open system by passing water-saturated gas over the octane phase until attainment of equilibrium. At which point, of course, the lid could be closed without any net changes occurring thereafter.

Would it be possible to obtain the same situation if we started out with a pure octane phase and added a saturated gas phase and closed the system?

The answer is **NO**. In this situation some of the water molecules from the gas phase had to partition into octane. Hence, the equilibrium gas phase concentration would be smaller than 100 % rh. Consequently the equilibrium water concentration in octane would then also be smaller than it was in equilibrium with 100 % rh.

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The quantitative answer to this problem is subject of chapter 3.



Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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c) Equilibrium partitioning of water (25°C)

What can you say about the equilibrium concentration of water in the gas phase in the following three phase system consisting of water, air and octane?

air $C_{\text{H}_2\text{O}}^0 = 0 \text{ mol/L}$ $C_{\text{H}_2\text{O}}^* = \text{[]} \text{ mol/L}$

water

$C_{\text{H}_2\text{O}}^0 = 55 \text{ mol/L}$
 $C_{\text{H}_2\text{O}}^* = \text{[]} \text{ mol/L}$

octane

$C_{\text{H}_2\text{O}}^0 = 0 \text{ mol/L}$
 $C_{\text{H}_2\text{O}}^* = \text{[]} \text{ mol/L}$

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CHECK

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

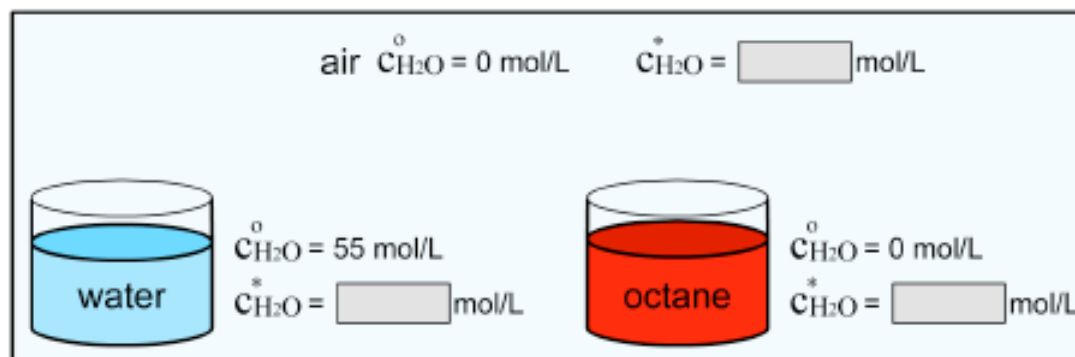
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c) Equilibrium partitioning of water (25°C)

Solution

The equilibrium concentration of water in the gas phase should of course not differ from that in the first figure. The only difference is that equilibrium will be achieved much faster here as water molecules do not have to diffuse through the octane film.



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No, unfortunately you are wrong ...

CHECK



Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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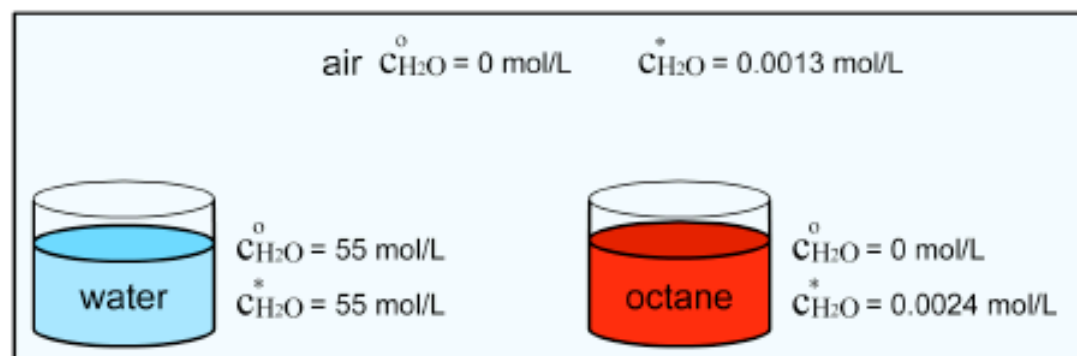
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c) Equilibrium partitioning of water (25°C)

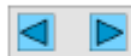
Here and before we have ignored the fact that octane molecules will also partition between all available phases. Does the partitioning of octane molecules affect the partitioning of water molecules?

yes

no



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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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c) Equilibrium partitioning of water (25°C)

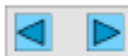
Solution

Octane will certainly partition into the gas phase in detectable quantities. But there will still be so few octane molecules in the gas phase (i.e., the concentration in the gas phase will be so low), that ideal-gas assumptions still hold. Recall that ideal gas conditions are given if intermolecular interactions between gas phase molecules are negligibly small. At the same time, octane will also partition into water. Again, the equilibrium concentration of octane in water will be so small that octane-saturated water (i.e., water in partition equilibrium with octane) may be treated as pure water. In other words, a chemical that partitions into the octane-saturated water phase is surrounded by and interacts with water molecules only.

In environmental chemistry the octanol/water partition constant of a chemical is a frequently used measure for its "hydrophobicity". Strictly spoken this is a partition constant between water saturated octanol and octanol saturated water. But the difference is hardly noticeable.

For some organic liquids other than octane, the situation can be completely different. If butanol instead of octane was used, then the butanol and water phases in equilibrium with one another (i.e., water saturated-butanol and butanol-saturated water) would differ substantially from their pure phases. As a consequence, the gas phase concentrations of water and butanol would also differ from the concentrations above the respective pure phases.

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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d) Equilibrium partitioning of benzene

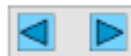
Below you see a closed system with an air and a water phase. Benzene is present in the system as well, at equilibrium partitioning between the two phases. Benzene is also present in the system but only at small concentrations.

The partition coefficient of benzene between air and water is:

$$K_{\text{air/water}} \text{ of benzene at } 25\text{ }^{\circ}\text{C} = 0.24\text{ L}_w/\text{L}_a$$



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Note, that this situation differs from a situation in which the starting concentration C_0 of benzene (before any partitioning to water could take place) is given.

Consistently throughout the text, we use the following notations to clearly distinguish these two situations: c^* stands for equilibrium concentrations; c^0 stands for initial (i.e., starting) concentrations, and c stands for the actual concentration in systems with unidentified equilibrium status.

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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d) Equilibrium partitioning of benzene

What can you say about the equilibrium concentration of benzene in the water phase in the middle and on the right?

1 L air, 1 L water, $c^* = 5 \text{ ng/L}$, $c' = 21 \text{ ng/L}$

1 L air, 1 L water, $c^* = 5 \text{ mmol/L}$, $c' = \text{[] mmol/L}$, CHECK

1 L air, 1 L water, $c^* = 5 \text{ ng/kg}$, $c' = \text{[] ng/kg}$, CHECK

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$K_{\text{air/water}}$ of benzene at 25 °C = 0.24 L_w/L_a

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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d) Equilibrium partitioning of benzene

What is the equilibrium water concentration if the water phase has a volume of two litres instead of one litre?

1 L air $c^* = 5 \text{ ng/L}$

1 L water $c^* = 21 \text{ ng/L}$

1 L air $c^* = 5 \text{ ng/L}$

2 L water $c^* = \text{[input box]} \text{ ng/L}$

CHECK

19/30

$K_{\text{air/water}}$ of benzene at $25^\circ\text{C} = 0.24 \text{ L}_w/\text{L}_a$

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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d) Equilibrium partitioning of benzene

What are the equilibrium concentrations of benzene in the air and in the water if 26 ng of benzene is added to the system?

1 L air $c^* = 5 \text{ ng/L}$
1 L water $c^* = 21 \text{ ng/L}$

add 26 ng benzene and mix thoroughly

1 L air $c^* = \text{[] ng/L}$
1 L water $c^* = \text{[] ng/L}$

CHECK

20/30

$K_{\text{air/water}}$ of benzene at 25 °C = 0.24 L_w/L_a

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".


Equilibrium partitioning of organic compounds

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e) Equilibrium between different phases(25°C)

Is equilibrium attained in this bottle ?



5 L air 25 ng benzene

1 L water 21 ng benzene

21/30

$K_{\text{air/water}}$ of benzene at 25 °C = 0.24 L_w/L_a

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

Equilibrium partitioning of organic compounds

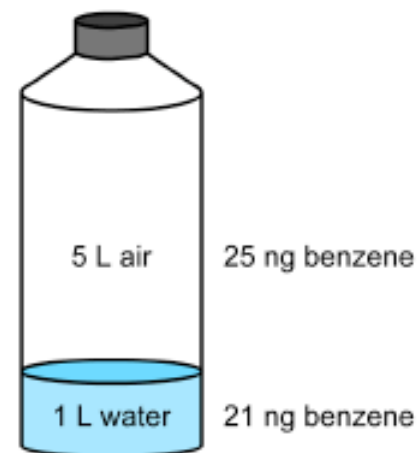
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e) Equilibrium between different phases(25°C)

Is equilibrium attained in this bottle ?

The correct answer is yes, the concentrations are the same as in the previous examples and they obey the reported partition constant. Note that the figure gives absolute masses of benzene of 25 ng and 21 ng in the gas and water phases, respectively. In order to compare these figures to the partition constant you first need to convert these to concentrations, using the volumes provided in the figure.



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 $K_{\text{air/water}}$ of benzene at 25 °C = 0.24 L_w/L_a

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

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f) Equilibrium partitioning of benzene

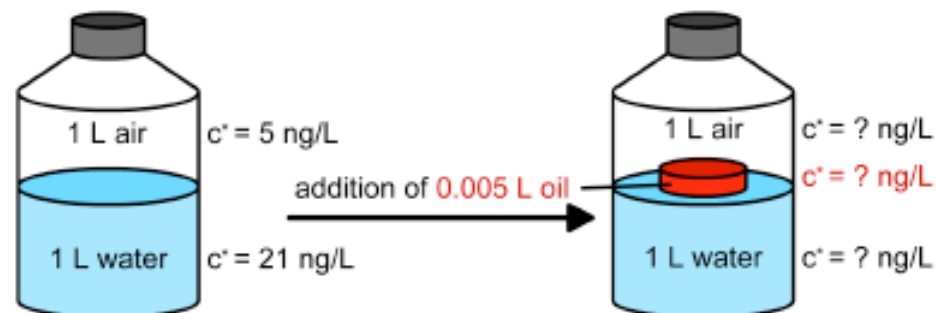
What happens to the equilibrium concentrations in the system when a third phase, e.g. oil, is added to the system?

Concentration in air and water will decrease

Concentration in air and water will increase

The concentrations stay the same

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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f) Equilibrium partitioning of benzene

Solution

Some of the benzene molecules present in the system will partition into the new oil phase. The equilibrium concentrations of benzene in water and air will therefore be lower than the respective concentrations in the initial system shown on the left.

You cannot give a quantitative answer unless you know the partition constant of benzene between water and oil or air and oil. This information is not provided in the figure.

Yes, your answer is correct!
However, please read carefully through the solution ...

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

[Equilibrium partitioning of organic compounds](#)

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f) Equilibrium partitioning of benzene

Solution

Some of the benzene molecules present in the system will partition into the new oil phase. The equilibrium concentrations of benzene in water and air will therefore be lower than the respective concentrations in the initial system shown on the left.

You cannot give a quantitative answer unless you know the partition constant of benzene between water and oil or air and oil. This information is not provided in the figure.

Knowing the water-oil partition constant, the new equilibrium concentrations of benzene are as follows: 3 ng_{benzene}/L_{air}, 2000 ng_{benzene}/L_{oil}, and 13 ng_{benzene}/L_{water} (the necessary calculations are explained in the next chapter).

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

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f) Equilibrium partitioning of benzene

Solution

Some of the benzene molecules present in the system will partition into the new oil phase. The equilibrium concentrations of benzene in water and air will therefore be lower than the respective concentrations in the initial system shown on the left.

You cannot give a quantitative answer unless you know the partition constant of benzene between water and oil or air and oil. This information is not provided in the figure.

Knowing the water-oil partition constant, the new equilibrium concentrations of benzene are as follows: $3 \text{ ng}_{\text{benzene}}/\text{L}_{\text{air}}$, $2000 \text{ ng}_{\text{benzene}}/\text{L}_{\text{oil}}$, and $13 \text{ ng}_{\text{benzene}}/\text{L}_{\text{water}}$ (the necessary calculations are explained in the next chapter).

Remember: The partition constant, i.e. the ratio of the equilibrium concentrations between two phases (e.g. air and water), is independent of (i) the presence of an additional phase(s) in the system, and (ii) the total mass of compound in the system (provided that we are still in the linear range of the partition isotherm). In contrast to the partition constant, the actual equilibrium concentrations –of course– depend on (i) and (ii).

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

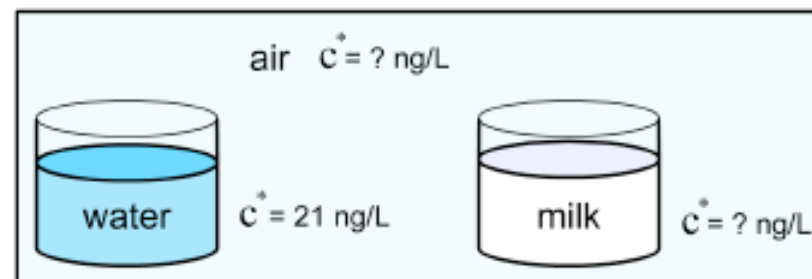
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g) Equilibrium partitioning of benzene

Can you say anything about the equilibrium partitioning of benzene into milk?



The equilibrium concentration of benzene in milk will be

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Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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g) Equilibrium partitioning of benzene

No, the equilibrium concentration of benzene in milk will be much higher

Solution

Milk contains ca. 4 volume% (i.e., 4% v/v) fat. It is reasonable to assume that the partition constant of benzene between water and fat is similar to the one between water and oil.

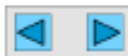
The equilibrium concentration in the aqueous fraction of the milk is approximately 21 ng_{benzene}/L_{water}. Given the result of the previous problem, $K_{\text{benzene, oil/water}} = 154$ (L_{water}/L_{oil}). The equilibrium concentration of benzene in the milk fat should thus be 3231 ng_{benzene}/L_{fat} (In the next chapter you will see how this is calculated).

The total concentration of benzene in milk –neglecting proteins and carbohydrates in the milk– is calculated as:

$$c^*_{\text{benzene in milk}} = 0.96 [\text{L}_{\text{water}}/\text{L}_{\text{milk}}] * 21 [\text{ng}_{\text{benzene}}/\text{L}_{\text{water}}] + 0.04 [\text{L}_{\text{oil}}/\text{L}_{\text{milk}}] * 3231 [\text{ng}_{\text{benzene}}/\text{L}_{\text{oil}}]$$

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$$= 150 [\text{ng}_{\text{benzene}}/\text{L}_{\text{milk}}]$$




Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).

Equilibrium partitioning of organic compounds

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h) Equilibrium partitioning of benzene



2 L air $c^0 = 21 \text{ ng/L}$ benzene in air

2 L water $c^* = ? \text{ ng/L}$ benzene in water

Questions:

Equilibrium concentrations in air and water in ng/L at 25°C?

Mass of benzene in air and water at equilibrium at 25°C in ng?

At what volume of air would 95% of the total amount of benzene reside in the air phase?

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◀ ▶

$K_{\text{air/water}}$ of benzene at 25 °C = 0.24 L_w/L_a

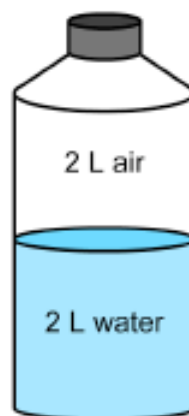
Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter "[A kinetic view on EP](#)".

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h) Equilibrium partitioning of benzene



$c^0 = 21 \text{ ng/L}$
benzene in air

$c^* = ? \text{ ng/L}$
benzene in water

Solution

In order to answer these questions, you first need to learn more about the working with partition constants in a quantitative manner. This is the focus of chapter 3.

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$K_{\text{air/water}}$ of benzene at $25^\circ\text{C} = 0.24 \text{ L}_w/\text{L}_a$

Simulate the situation on page 7/30 with the [virtual experiment](#) in the subchapter ["A kinetic view on EP"](#).