

Answers to Exercise 8.2

Henry's Law and Raoult's Law

1.

- (a) Henry's law is $[A] = k_H P_A$. It relates the concentration of substance A in solution, $[A]$, to the vapour pressure of that substance above the solution, P_A . k_H is the Henry's law constant, and is therefore a constant for any particular combination of gas and liquid.

As the vapour pressure of the substance A above the solution increases, the concentration of A in solution increases proportionally (and vice versa). So, increasing the amount of gas above the solution makes more of the gaseous substance dissolve.

- (b) Raoult's law is $P_A = X_A P_A^\circ$. It relates the vapour pressure (of solvent), P_A , above a solution to the mole fraction of solvent, X_A , in solution. P_A° is the vapour pressure above a pure sample of that liquid, and is therefore a constant for any particular liquid.

As the mole fraction of solvent in solution increases, the vapour pressure above the solution increases proportionally. So, adding more solute to the solution (decreasing the fraction of solution that is solvent) decreases the vapour pressure of the solvent above the solution.

There is more detail in these answers than necessary to answer the question. The added detail is intended to clearly differentiate between the two laws.

2.

- (a) The solubility of each gas in water appears to decrease as temperature is increased. The values for the Henry's law constants for each gas decrease as temperature increases.

Since $[A] = k_H P_A$, if P_A is held constant, $[A]$ decreases as k_H decreases.

- (b) Carbon dioxide (CO_2) has the highest solubility in water at 25 °C because it has the largest value for k_H at 25 °C.

Since $[A] = k_H P_A$, if P_A is held constant, $[A]$ increases as k_H increases.

3.

- (a) Raoult's law can be used to calculate the equilibrium vapour pressure of water above a solution in which the solvent is water (like salt water). For this calculation, you need to know the mole fraction of water in the salt water and the vapour pressure above pure water.

- (b) Neither law is applicable to this situation since there is no gas-liquid equilibrium involved.

- (c) Henry's law can be used to calculate the concentration of dissolved gas if the pressure of that gas above the solution is known. For this calculation, you need to know the relevant Henry's law constant and the atmospheric pressure of oxygen.

- (d) Neither law is applicable to this situation. Raoult's law refers to vapour pressure of the solvent above a solution – not a pure liquid.

4. *Because this question is about the relationship between the vapour pressure above a pure liquid (water) and a solution in which that liquid is the solvent (sugar-water), it can be answered using Raoult's law.*

Step 1: Calculate the molar masses of sucrose and water

$$M_{C_{12}H_{22}O_{11}} = 12 \left(12.011 \frac{g}{mol} \right) + 22 \left(1.0079 \frac{g}{mol} \right) + 11 \left(15.9994 \frac{g}{mol} \right) = 342.299 \frac{g}{mol}$$

$$M_{H_2O} = 2 \left(1.0079 \frac{g}{mol} \right) + \left(15.9994 \frac{g}{mol} \right) = 18.0152 \frac{g}{mol}$$

Step 2: Calculate the moles of each species in solution

$$n_{C_{12}H_{22}O_{11}} = 45 g \times \frac{1 mol}{342.299 g} = 0.13 mol$$

$$n_{H_2O} = 250 g \times \frac{1 mol}{18.0152 g} = 13.9 mol$$

Step 3: Calculate the mole fraction of water in the sugar-water solution

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{C_{12}H_{22}O_{11}}} = \frac{13.9 mol}{13.9 mol + 0.13 mol} = 0.991$$

Step 4: Use Raoult's law to calculate the vapour pressure of water above the sugar-water solution

$$P_{\text{water over sugar-water}} = X_{\text{water in sugar-water}} P_{\text{pure water}}$$

$$P_{\text{water over sugar-water}} = (0.991)(0.0317 \text{ bar})$$

$$P_{\text{water over sugar-water}} = 0.0314 \text{ bar}$$

Step 5: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The sugar-water solution is primarily sugar, so it makes sense that the pressure of water vapour above it is almost as much as it would be over pure water.

5. *Because this question is about the relationship between the pressure of a gas and the concentration of that gas dissolved in a solvent, it can be answered using Henry's law.*

(a) **Step 1: Convert the pressure into bar**

$$p_{\text{CO}_2} = 30 \text{ psi} \times \frac{1 \text{ bar}}{14.5 \text{ psi}} = 2.069 \text{ bar} = 2.1 \text{ bar}$$

Step 2: Identify the appropriate Henry's law constant

$$k_H = 0.077 \frac{\text{mol}}{\text{L}\cdot\text{bar}} \text{ for the } 0^\circ\text{C calculation}$$

$$k_H = 0.034 \frac{\text{mol}}{\text{L}\cdot\text{bar}} \text{ for the } 25^\circ\text{C calculation}$$

Step 3: Use Henry's law to calculate the concentration of dissolved carbon dioxide when equilibrium is reached

$$[A] = k_H P_A = \left(0.077 \frac{\text{mol}}{\text{L}\cdot\text{bar}}\right) (2.1 \text{ bar}) = 0.16 \frac{\text{mol}}{\text{L}} \text{ at } 0^\circ\text{C}$$

$$[A] = k_H P_A = \left(0.034 \frac{\text{mol}}{\text{L}\cdot\text{bar}}\right) (2.1 \text{ bar}) = 0.070 \frac{\text{mol}}{\text{L}} \text{ at } 25^\circ\text{C}$$

Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

Step 5: Answer the question

As shown above, the solubility of carbon dioxide in water is lower at the higher temperature, so cold water can dissolve more carbon dioxide than warm water.

- (b) You cannot do this calculation with the information provided.

Henry's law constants are solvent-dependent. The only Henry's law constants provided in this Exercise are for water as a solvent. To do this calculation, you would need a value for the Henry's law constant for gin (or a mixture of alcohol and water approximating gin).