

17.4: The Vapor Pressures of Solutions

Learning Objectives

- To understand how Temperature, Pressure, and the presence of other solutes affect the solubility of solutes in solvents.

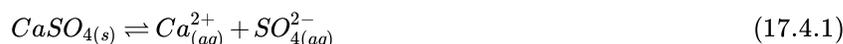
Solubility is defined as the upper limit of solute that can be dissolved in a given amount of solvent at equilibrium. In such an equilibrium, [Le Chatelier's principle](#) can be used to explain most of the main factors that affect solubility. Le Châtelier's principle dictates that the effect of a stress upon a system in chemical equilibrium can be predicted in that the system tends to shift in such a way as to alleviate that stress.

Solute-Solvent Interactions Affect Solubility

The relation between the solute and solvent is very important in determining **solubility**. Strong solute-solvent attractions equate to greater solubility while weak solute-solvent attractions equate to lesser **solubility**. In turn, polar solutes tend to dissolve best in polar solvents while non-polar solutes tend to dissolve best in non-polar solvents. In the case of a polar solute and non-polar solvent (or vice versa), it tends to be insoluble or only soluble to a miniscule degree. A general rule to remember is, "Like dissolves like."

Common-Ion Effect

The [common-ion effect](#) is a term that describes the decrease in **solubility** of an ionic compound when a salt that contains an ion that already exists in the chemical equilibrium is added to the mixture. This effect best be explained by [Le Chatelier's principle](#). Imagine if the slightly soluble ionic compound calcium sulfate, CaSO_4 , is added to water. The net ionic equation for the resulting chemical equilibrium is the following:



Calcium sulfate is slightly soluble; at equilibrium, most of the calcium and sulfate exists in the solid form of calcium sulfate.

Suppose the soluble ionic compound copper sulfate (CuSO_4) were added to the solution. Copper sulfate is soluble; therefore, its only important effect on the net ionic equation is the addition of more sulfate (SO_4^{2-}) ions.



The sulfate ions dissociated from copper sulfate are already present (common to) in the mixture from the slight dissociation of calcium sulfate. Thus, this addition of sulfate ions places stress on the previously established equilibrium. Le Chatelier's principle dictates that the additional stress on this product side of the equilibrium results in the shift of equilibrium towards the reactants side in order to alleviate this new stress. Because of the shift toward the reactant side, the solubility of the slightly soluble calcium sulfate is reduced even further.

Temperature Affects Solubility

Temperature changes affect the solubility of solids, liquids and gases differently. However, those effects are finitely determined only for solids and gases.

Solids

The effects of temperature on the solubility of solids differ depending on whether the reaction is endothermic or exothermic. Using Le Chatelier's principle, the effects of temperature in both scenarios can be determined.

- First, consider an **endothermic** reaction ($\Delta H_{\text{solvation}} > 0$): Increasing the temperature results in a stress on the reactants side from the additional heat. Le Chatelier's principle predicts that the **system shifts toward the product side** in order to alleviate this stress. By shifting towards the product side, more of the solid is dissociated when equilibrium is again established, resulting in **increased** solubility.
- Second, consider an **exothermic** reaction ($\Delta H_{\text{solvation}} < 0$): Increasing the temperature results in a stress on the products side from the additional heat. Le Chatelier's principle predicts that the **system shifts toward the reactant side** in order to alleviate this stress. By shifting towards the reactant's side, less of the solid is dissociated when equilibrium is again established, resulting in **decreased** solubility.

Liquids

In the case of liquids, there is no defined trends for the effects of temperature on the solubility of liquids.

Gases

In understanding the effects of temperature on the solubility of gases, it is first important to remember that temperature is a measure of the average kinetic energy. As temperature increases, kinetic energy increases. The greater kinetic energy results in greater molecular motion of the gas particles. As a result, the gas particles dissolved in the liquid are more likely to escape to the gas phase and the existing gas particles are less likely to be dissolved. The converse is true as well. The trend is thus as follows: increased temperatures mean lesser solubility and decreased temperatures mean higher solubility.

Le Chatelier's principle allows better conceptualization of these trends. First, note that the process of dissolving gas in liquid is usually **exothermic**. As such, **increasing** temperatures result in stress on the product side (because heat is on the product side). In turn, Le Chatelier's principle predicts that the system shifts towards the reactant side in order to alleviate this new stress. Consequently, the equilibrium concentration of the gas particles in gaseous phase increases, resulting in **lowered** solubility.

Conversely, **decreasing** temperatures result in stress on the reactant side (because heat is on the product side). In turn, Le Chatelier's principle predicts that the system shifts toward the product side in order to compensate for this new stress. Consequently, the equilibrium concentration of the gas particles in gaseous phase would decrease, resulting in **greater** solubility.

Pressure Affects Solubility of Gases

The effects of pressure are only significant in affecting the solubility of gases in liquids.

- **Solids & Liquids:** The effects of pressure changes on the solubility of solids and liquids are negligible.
- **Gases:** The effects of pressure on the solubility of gases in liquids can best be described through a combination of [Henry's law](#) and Le Chatelier principle. Henry's law dictates that when temperature is constant, the solubility of the gas corresponds to its partial pressure. Consider the following formula of Henry's law:

$$p = k_h c \quad (17.4.3)$$

where:

- p is the partial pressure of the gas above the liquid,
- k_h is Henry's law constant, and
- c is the concentrate of the gas in the liquid.

This formula indicates that (at a constant temperature) when the partial pressure decreases, the concentration of gas in the liquid decreases as well, and consequently the solubility also decreases. Conversely, when the partial pressure increases in such a situation, the concentration of gas in the liquid will increase as well; the solubility also increases. Extending the implications from [Henry's law](#), the usefulness of Le Chatelier's principle is enhanced in predicting the effects of pressure on the solubility of gases.

Consider a system consisting of a gas that is partially dissolved in liquid. An increase in pressure would result in greater partial pressure (because the gas is being further compressed). This increased partial pressure means that more gas particles will enter the liquid (there is therefore less gas above the liquid, so the partial pressure decreases) in order to alleviate the stress created by the increase in pressure, resulting in greater solubility.

The converse case in such a system is also true, as a decrease in pressure equates to more gas particles escaping the liquid to compensate.

✓ Example 1

Consider the following exothermic reaction that is in equilibrium



What will happen to the solubility of the carbon dioxide if:

- Temperature is increased?
- Pressure and temperature are increased?
- Pressure is increased but temperature is decreased?
- Pressure is increased?

Solution

- The reaction is exothermic, so an increase in temperature means that solubility would decrease.
- The change in solubility cannot be determined from the given information. Increasing pressure increased solubility, but increasing temperature decreases solubility
- An increase in pressure and an increase in temperature in this reaction results in greater solubility.
- An increase in pressure results in more gas particles entering the liquid in order to decrease the partial pressure. Therefore, the solubility would increase.

✓ Example 2: The Common Ion Effect

Bob is in the business of purifying silver compounds to extract the actual silver. He is extremely frugal. One day, he finds a barrel containing a saturated solution of silver chloride. Bob has a bottle of water, a jar of table salt (NaCl(s)), and a bottle of vinegar (CH_3COOH). Which of the three should Bob add to the solution to maximize the amount of solid silver chloride (minimizing the solubility of the silver chloride)?

Solution

Bob should add table salt to the solution. According to the common-ion effect, the additional Cl^- ions would reduce the solubility of the silver chloride, which maximizes the amount of solid silver chloride.

✓ Example 3:

Allison has always wanted to start her own carbonated drink company. Recently, she opened a factory to produce her drinks. She wants her drink to "out-fizz" all the competitors. That is, she wants to maximize the solubility of the gas in her drink. What conditions (high/low temperature, high/low pressure) would best allow her to achieve this goal?

Solution

She would be able to maximize the solubility of the gas, (CO_2 in this case, in her drink (maximize fizz) when the pressure is high and temperature is low.

✓ Example 4

Butters is trying to increase the solubility of a solid in some water. He begins to frantically stir the mixture. Should he continue stirring? Why or why not?

Solution

He stop stop stirring. Stirring only affects how fast the system will reach equilibrium and does not affect the solubility of the solid at all.

✓ Example 5: Outgassing Soda

With respect to Henry's law, why is it a poor ideal to open a can of soda in a low pressure environment?

Solution

The fizziness of soda originates from dissolved CO_2 , partially in the form of carbonic acid. The concentration of CO_2 dissolved in the soda depends on the amount of ambient pressure pressing down on the liquid. Hence, the soda can will be under pressure to maintain the desired CO_2 concentration. When the can is opened to a lower pressure environment (e.g., the ambient atmosphere), the soda will quickly "outgas" (CO_2 will come out of solution) at a rate depending on the surrounding atmospheric pressure. If a can of soda were opened under a lower pressure environment, this outgassing will be faster and hence more explosive (and dangerous) than under a high pressure environment.

Terms

- The **solubility** of a solute is the concentration of the saturated solution.
- A **saturated solution** a solution in which the maximum amount of solute has dissolved in the solvent at a given temperature.
- An **unsaturated solution** a solution in which the solute has completely dissolved in the solvent.
- A **supersaturated solution** is a solution in which the amount of solute dissolved under given conditions exceeds its supposed upper limit.
- **Le Châtelier's principle** states that when a system in chemical equilibrium is stressed, the system will shift in a way that alleviates the stress.
- **Endothermic reaction:** a reaction in which heat is absorbed ($\Delta H > 0$)
- **Exothermic reaction:** a reaction in which heat is released ($\Delta H < 0$)

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