BAE 820 Physical Principles of Environmental Systems

## Henry's Law - Raoult's Law – Partition law

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Henry's law

- At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

$$P_i = K_H C_i$$

- Where P_i is the partial pressure of the gaseous solute above the solution, C_i is the concentration of the dissolved gas and K_H is Henry's constant with the dimensions of pressure divided by concentration. K_H is different for each solute-solvent pair.
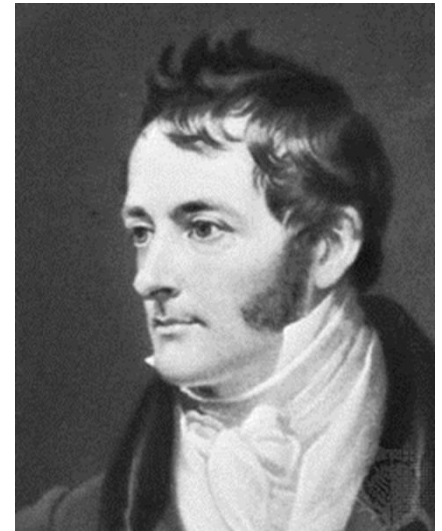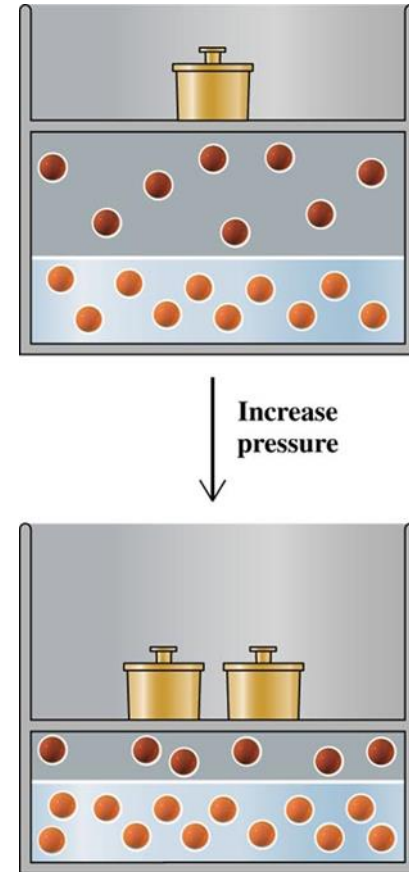

William Henry

(1774-1836)

Henry's law

For a gas mixture, Henry's law helps to predict the amount of each gas which will go into solution. When a gas is in contact with the surface of a liquid, the amount of the gas which will go into solution is proportional to the partial pressure of that gas.
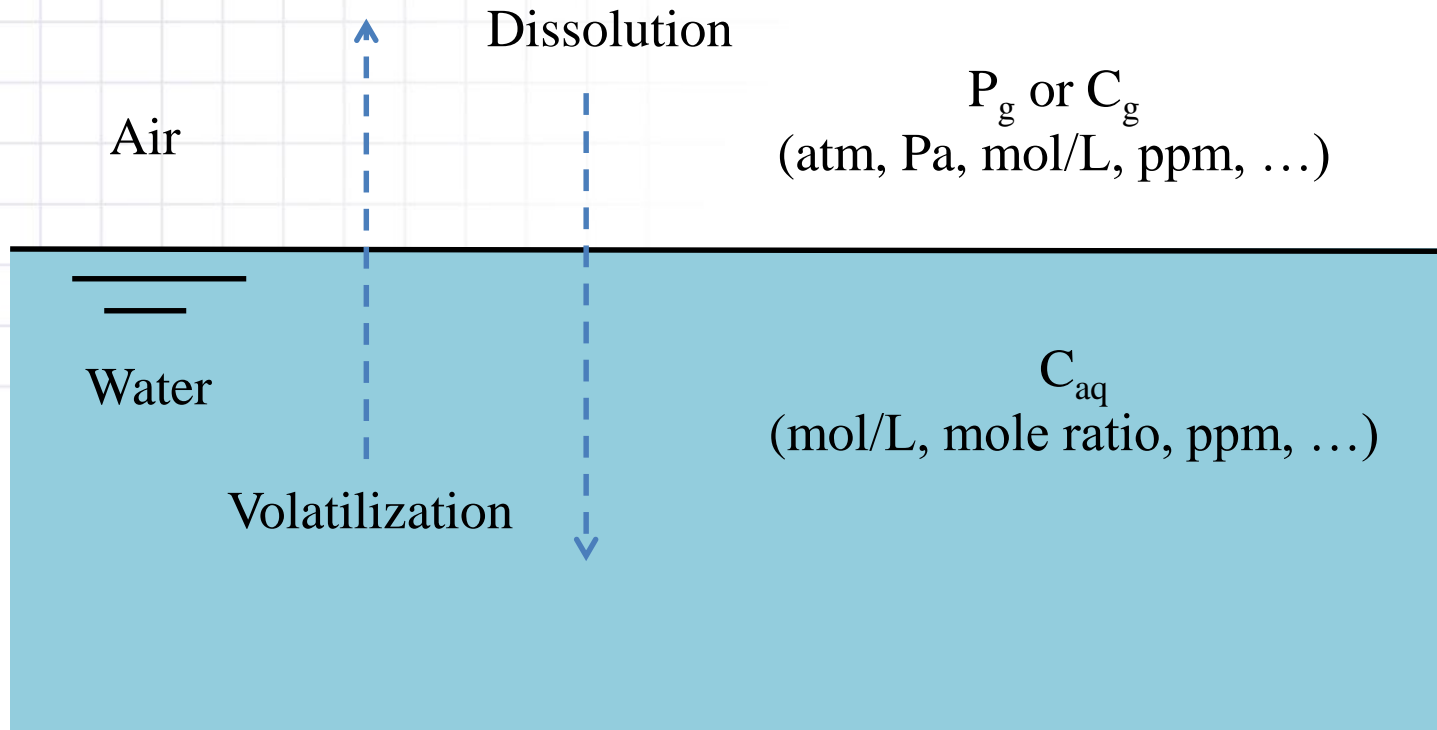
An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. the solubility of gases generally decreases with increasing temperature.

A simple rationale for Henry's law is that if the partial pressure of a gas is twice as high, then on the average twice as many molecules will hit the liquid surface in a given time interval,

Increase pressure

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Air-water equilibrium

Dissolution

Air

P_g or C_g
(atm, Pa, mol/L, ppm, …)

At equilibrium,

$$K_H = \frac{P_g}{C_{aq}}$$

Water

C_{aq}
(mol/L, mole ratio, ppm, …)

Volatilization

Various units of the Henry's constant (gases in water at 25ºC)

Form of equation	$K_{H, pc}=P/C_{aq}$	$K_{H, cp}=C_{aq}/P$	$K_{H, px}=P/x$	$K_{H, cc}=C_{aq}/C_{gas}$
Units	L·atm/mol	mol/(L·atm)	atm	dimensionless
O_2	769	1.3×10^{-3}	4.26×10^{4}	3.18×10^{-2}
N_2	1639	6.1×10^{-4}	9.08×10^{4}	1.49×10^{-2}
CO_2	29	3.4×10^{-2}	1.63×10^{3}	0.832

Since all K_H may be referred to as Henry's law constants, we must be quite careful to check the units, and note which version of the equation is being used.

Unit conversions

$$K_{H,\,pc} = \frac{1}{K_{H,\,cp}}$$

$$\frac{K_{H,\,px}}{[atm]} = \frac{1000}{18} \times \frac{K_{H,\,pc}}{[atm/M]} = 55 \times \frac{K_{H,\,pc}}{[atm/M]}$$

At 298K,

$$\frac{K_{H,\,pc}}{[atm/M]} = \frac{RT}{K_{H,\,cc}} = \frac{0.082 \times 298}{K_{H,\,cc}} = \frac{24.4}{K_{H,\,cc}}$$

Henry's constant

Except for high soluble gases such as NH_3 where Henry's law constant varies slightly with concentration level in solution, the solubility curves for most less soluble gases are straight lines and obey Henry's law.

	K_H (atm/M) in water at 25°C
O_2	769
N_2	1639
CO_2	29
NH_3	0.013 to 0.019
H_2S	10
SO_2	0.8
CH_4	714

Solubility and Henry's law constant

Solubility: the amount of a substance that will dissolve in a given amount of solvent, g/L.

A saturated solution is one which is in equilibrium with undissolved solute – it has reached limit of solubility. According to Henry's law, gases are more soluble at higher pressure.

The solubility

$$S_g = P_g / K_H$$

Raoult's law

- Partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

$$P_i = P_{i0}X_i$$

- Where P_i is the partial pressure of the gaseous solute i above the solution, P_{i0} is the vapor pressure of the pure component i, and X_i is the mole fraction of the component i in the solution.

- When solution concentration is low ($X_i \rightarrow 0$) , Henry's law is applicable. Henry's law is only applicable to gas solute mole fractions less than 0.03.

Francois-Marie Raoult
(1830-1901)

Vapor pressure

- When a liquid comes in contact with the air, a fraction of it will go into vapor phase and mix with the air. If the liquid is a pure substance, the partial pressure at equilibrium is called vapor pressure.

- Higher vapor pressure means higher potential of volatilization (vaporization). Vapor pressure increases with increasing temperature, and for organic molecules, it may be estimated from molecular structure. Generally, vapor pressure increases with decreasing molecular weight.

	Vapor pressure at 25ºC (kPa)
Water	3.17
NH_3	1003
H_2S	2026
CO_2	6401

Raoult's law

When a substance is dissolved in a solution, the vapor pressure of the solution will generally decrease. The vapor pressure of a solution is lower than that of the pure solvent.

The partial pressure of a solvent vapor in equilibrium with a solution is proportional to the ratio of the number of solvent molecules to non-volatile solute molecules.


Vapor pressure

Solvent alone

(a)

Vapor pressure

Solvent + solute

(b)
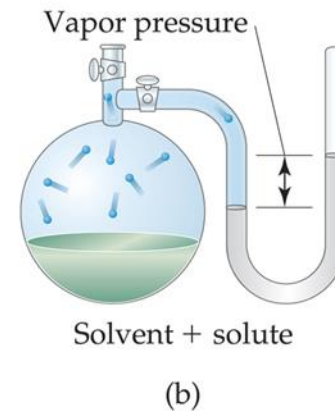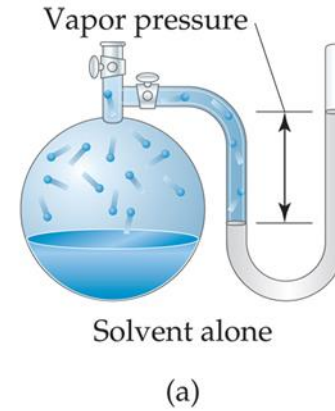
Two opposite ends of the composition range

Raoult's law and Henry's law apply at opposite ends of the composition range. Both laws are limit laws.

- Raoult's law: $\lim\limits_{x \to 1} \left(\dfrac{P_i}{X_i} \right) = Pi_0$

- Henry's law: $\lim\limits_{x \to 0} \left(\dfrac{P_i}{C_i} \right) = K_H$

Henry's law can be used to describe a minority component and Raoult's law can be used to describe a majority component.

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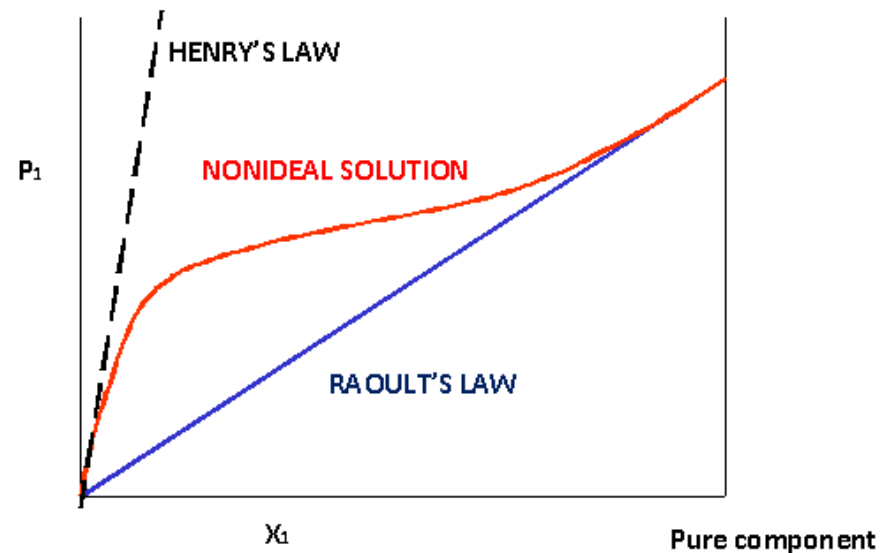
The van 't Hoff equation

When the temperature of a system changes, the Henry constant will also change. This is why some people prefer to name it Henry coefficient.

$$\frac{dlnK_{eq}}{d\frac{1}{T}} = \frac{\Delta H}{R}$$

In which, K_{eq} is the equilibrium constant; ΔH is the reaction enthalpy; R is the gas constant.

$$K_{H,\,pc}(T) = K_{H0,\,pc}\exp[-C(1/T-1/298)]$$

Where $K_{H0,\,pc}$ is $K_{H,\,pc}$ at the standard temperature (298K), C is a constant in Kelvins. For O_2, C=1700K.

For NH_3/water solution, C=3670K. A simplified equation is
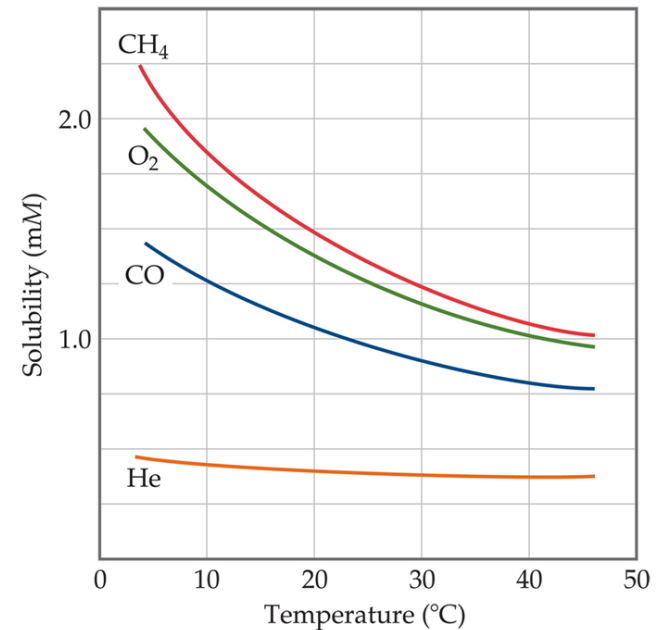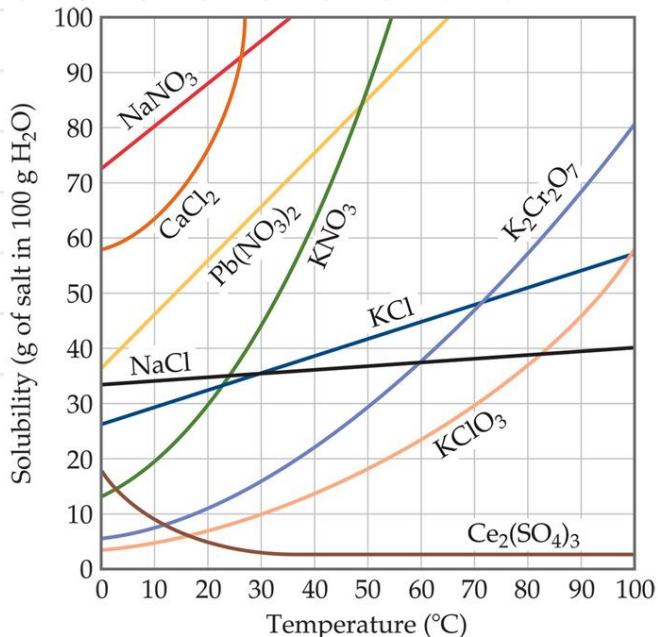
$$K_{H,\,pc}(T) = 1000\exp(3.133-4200/T)$$

J.H. van't Hoff
(1852-1911)

The first winner of Noble Prize in Chemistry (1901)

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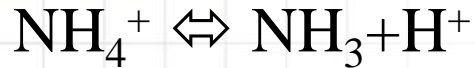# Solubility and temperature

Solids solubility usually increases as T increases.

Gas solubility almost always decreases as T increases ($K_{H, pc}$ increases)

That is why sometimes in the summer there are some fish kills due to the warmer water and less oxygen available for the fish.
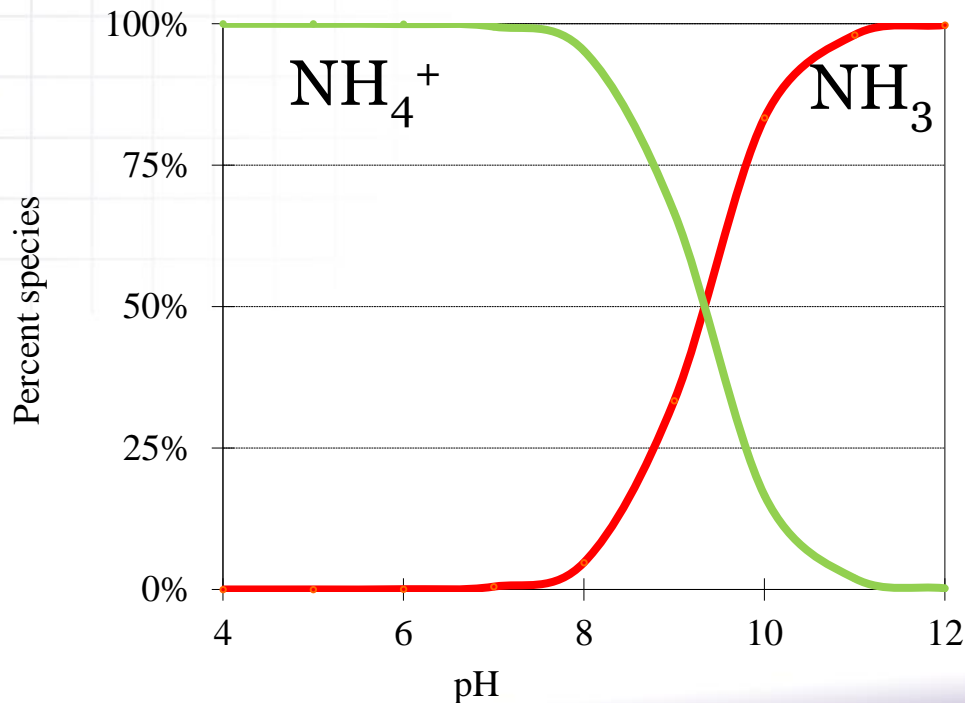
Influence of pH on NH$_3$

$NH_4^+ \Leftrightarrow NH_3 + H^+$

$K_a = [NH_3][H^+] / [NH_4^+]$

$[NH_3] / [NH_4^+] = K_a / [H^+]$

For NH$_3$, at 25ºC, pK$_a$=9.3

Influence of pH H$_2$S

$H_2S \Leftrightarrow H^+ + HS^-$

$K_a = [H^+][HS^-]/[H_2S]$

$[H_2S]/[HS^-]=[H^+]/K_a$

For H$_2$S, at 25ºC, pK$_a$=7.1
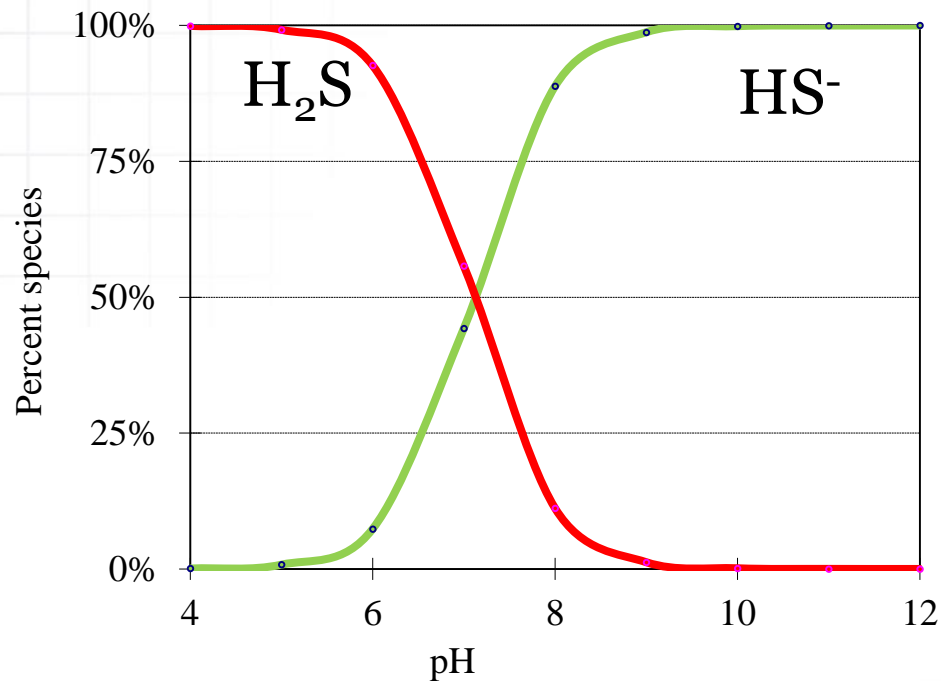
Partitioning equilibrium between two immiscible solvents

The word "partition" means a substance is distributed between two phases (or two immiscible solvents) in a dynamic equilibrium. The ratio of the concentrations of a solute in two immiscible solvents (solvent 1 and solvent 2) is constant when equilibrium has been reached. This constant is known as the partition coefficient, $K_{partition}$.

$$K_{partition} = \frac{Concentration\ of\ solute\ in\ solvent\ 1}{Concentration\ of\ solute\ in\ solvent\ 2}$$

The partition law holds true for dilute solutions. For concentrated solutions, interactions between solvent and solute have to be considered and the concentration terms should be expressed by "activity".
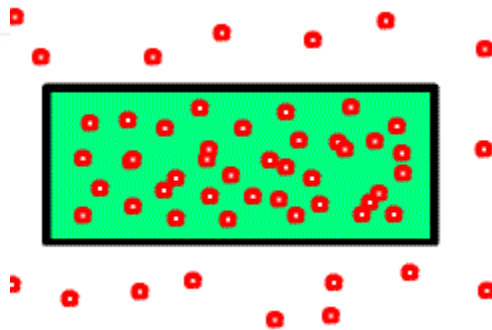
Absorption vs. Adsorption

Absorption is the process in which a fluid permeates or is dissolved by a liquid or a solid (absorbent).

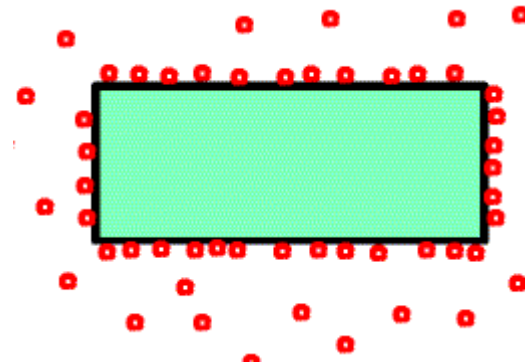Absorption is a bulk process which involves the whole volume of the material.

Adsorption is the adhesion of atoms, ions, or molecules to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.

Adsorption is a surface-based process.

Absorption

Adsorption

Partitioning between liquid and solid phases

- Freundlich isotherm

$$\frac{x}{m} = Kc^{1/n}$$

- Langmuir isotherm

$$\frac{x}{m} = \frac{Q_0 bc}{1 + bc}$$

Where,

x is the quantity adsorbed.

m is the mass of adsorbent (solid).

K is the Freundlich partition coefficient.

c is the equilibrium concentration of adsorbate in solution..

1/n is the Freundlich exponent. For solutions with low concentrations, $1/n \approx 1$ (linear isotherm).

Q_0 is the maximum adsorption at fixed temperature.

b is the Langmuir adsorption constant constant related to net enthalpy of adsorption.

Freundlich isotherm is widely used for NH_4^+ partition between liquid and solid phase.

Problem solving #5-1

- The lowest level of oxygen gas dissolved in water that will support life is ~ 1.3×10^{-4} mol/L. Calculate the solubility of oxygen in water at 25ºC. At the normal atmospheric pressure of oxygen, is there adequate oxygen in water to support life?

- Given: The Henry's law constant for oxygen in water is 769 atm/M, or 1.3×10^{-3} mol/L/atm.

Problem solving #5-2

- How many grams of carbon dioxide gas is dissolved in a 1 L bottle of carbonated water if the manufacturer uses a pressure of 2.4 atm in the bottling process at 25 °C?

- Given: K_H of CO_2 in water = 29 atm/(mol/L) at 25 °C

Problem #3-3

- In a preliminary study, you added 10 mL of the compound to 1 L of waste which resulted in the pH of the waste being reduced from 8.5 to 5.5. The untreated waste has total ammoniacal-N $[NH_3+NH_4^+]$ concentration of 250 mgN/L and $[H_2S+HS^-]$ of 5 mg/L.
- What are the changes in NH_3 and H_2S concentrations (based on theory) in the waste before and after application of the amendment?
- Given $pK_a=7.1$ for H_2S, $pK_a=9.3$ for NH_3

Problem solution #5-1

- Partial pressure of oxygen gas in the atmosphere is 21%, or 0.21 atm.

$$S_{oxygen} = P_g / K_H = 0.21/769 = 2.7 \times 10^{-4} \text{ mol/L}$$

Adequate to sustain life in water!

Problem solution #5-2

$C = P_g / K_H = 2.4 \text{ atm}/29 \text{ atm}/(\text{mol/L}) = 0.08 \text{ mol/L}$

g of CO_2 = 0.08 mol × 44 g/mol = 3.52 g

Problem #3-3

For NH_3, $pK_a = 9.3$

$[NH_4^+] = [NH_3][H^+]/10\wedge(-9.3)$

$[NH_3]*14/17 + [NH_4^+]*14/18 = 250$

So,

$[NH_3]*14/17 + [NH_3][H^+]/10\wedge(-9.3)*14/18 = 250$

$[NH_3] = 250/\{14/17 + [H^+]/10\wedge(-9.3)*14/18\}$

For H2S, $pK_a = 7.1$

$[HS^-] = [H_2S]*10\wedge(-7.1)/[H^+]$

$[H_2S] + [HS^-] = 5$

So,

$[H_2S] + [H_2S]*10\wedge(-7.1)/[H^+] = 5$

$[H_2S] = 5/\{1 + 10\wedge(-7.1)/[H^+]\}$

Problem #3-3

Before application of the amendment, pH=8.5,

$[NH_3]=250/\{14/17+10^{\wedge}(-8.5)/10^{\wedge}(-9.3)*14/18\}=43.62$ mg/L

$[H_2S]=5/\{1+10^{\wedge}(-7.1)/10^{\wedge}(-8.5)\}=0.19$ mg/L

After application of the amendment, pH=5.5,

$[NH_3]=250/\{14/17+10^{\wedge}(-5.5)/10^{\wedge}(-9.3)*14/18\}=0.51$ mg/L

$[H_2S]=5/\{1+10^{\wedge}(-7.1)/10^{\wedge}(-5.5)\}=4.88$ mg/L

So, after application of the amendment, NH_3 concentration is reduced from 43.62 mg/L to 0.51 mg/L. However, H_2S concentration increased from 0.19 mg/L to 4.88 mg/L.