Solution – Series 1 – Dissolved gas in liquids

Exercise 1:

Consider a vessel filled with $1\ L$ of water in CO_2 atmosphere at $2.5\ atm$. Calculate the mass of dissolved CO_2 when the temperature of the system is $25°C$. Henry's constant for carbon dioxide in water at $25°C$ is $3.36 \times 10^{-2}\ mol/(L.atm)$. The molar mass of CO_2 is $44.009\ g/mol$.

Applying Henry's law, the molar concentration of carbon dioxide dissolved in water is:

$$c_{CO_2} = H_{CO_2} p^*_{CO_2} = 3.36 \times 10^{-2}\ \frac{mol}{L.atm} \times\ 2.5\ atm = 0.084\ mol/L$$

Having $V = 1\ L$ of water, the number of moles of carbon dioxide dissolved in water is:

$$n_{CO_2} = c_{CO_2} V =\ 0.084\ mol$$

The mass of carbon dioxide dissolved in water is therefore:

$$m_{CO_2} = n_{CO_2} M_{CO_2} = 0.084\ mol \times 44.009 \frac{g}{mol} = 3.7g$$

Exercise 2:

Knowing that the mass concentration $c_{m,1}$ of a generic gas in solution at partial pressure $p_1^* = 150\ mmHg$ is $4.4\ g/L$, compute its mass concentration $c_{m,2}$ in the same solution when its partial pressure $p_2^* = 56\ mmHg$. The temperature is the same in both cases.

Equating Henry's constant at two different partial pressures:

$$H = \frac{c_{m,1}}{p_1^*} = \frac{c_{m,2}}{p_2^*}$$

One obtains:

$$c_{m,2} = c_{m,1} \frac{p_2^*}{p_1^*} = 4.4 \frac{g}{L} \times \frac{56\ mmHg}{150\ mmHg} = 1.64\ \frac{g}{L}$$

Exercise 3:

Table 1- Constants of equation 1 for different gases

Name	Formula	A	B	C	D	T range, K
Acetylene	C_2H_2	−156.51	8,160.2	21.403	0	274–343
Carbon dioxide	CO_2	−159.854	8,741.68	21.6694	−1.10261E-03	273–353
Carbon monoxide	CO	−171.764	8,296.9	23.3376	0	273–353
Ethane	C_2H_6	−250.812	12,695.6	34.7413	0	275–323
Ethylene	C_2H_4	−153.027	7,965.2	20.5248	0	287–346
Helium	He	−105.9768	4,259.62	14.0094	0	273–348
Hydrogen	H_2	−125.939	5,528.45	16.8893	0	273–345
Methane	CH_4	−338.217	13,282.1	51.9144	−0.0425831	273–523
Nitrogen	N_2	−181.587	8,632.13	24.7981	0	273–350
Oxygen	O_2	−171.2542	8,391.24	23.24323	0	273–333

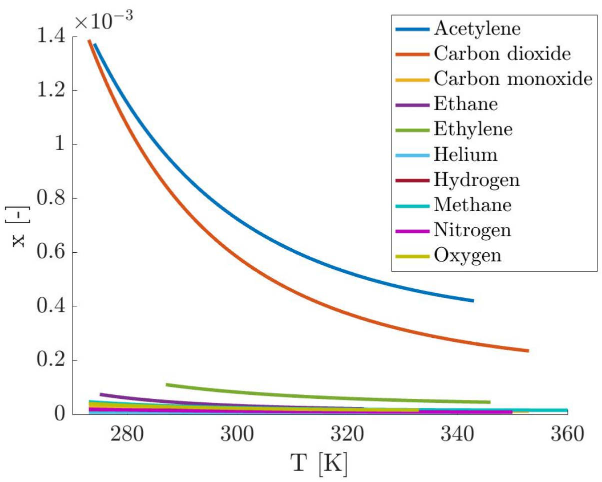
Table 2: Henry's constant for air [H]=[atm^{-1}]

T [°C]	0	5	10	15	20	25	30	35
10^{-4} x H	0,23	0,20	0,18	0,16	0,15	0,14	0,13	0,12
T [°C]	40	45	50	60	70	80	90	100
10^{-4} x H	0,11	0,11	0,11	0,10	0,10	0,09	0,09	0,09

1. Using Table 1 and equation 1 provided below, plot the evolution of the molar fraction of the gases listed in the table, when dissolved in water as a function of temperature.

$$\ln(x) = A + \frac{B}{T} + C\ln(T) + DT \qquad (1)$$

where T is expressed in Kelvin and x is the molar fraction of the solute dissolved in water when its partial pressure is 1 atm.



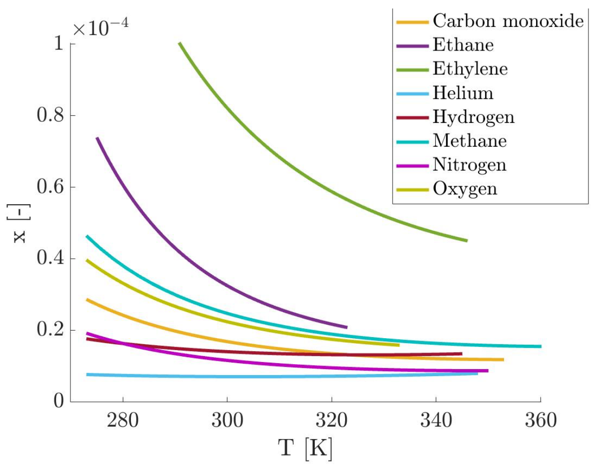


Figure 1: Solubility (molar fraction) of gases as function of temperature (Right: Zoom of Left graph)

2. Compute the Henry's constant for all listed gases at $25°C$.

$$H(T) = \frac{x(T)}{p^*} \; [atm^{-1}]$$

At $T = 25\ °C = 298.15\ K$, the Henry's constants for the different gases are:

- Acetylene: $H(T = 25°C) = 7.50 \times 10^{-4}\, atm^{-1}$
- Carbon dioxide: $H(T = 25°C) = 6.12 \times 10^{-4}\, atm^{-1}$
- Carbon monoxide: $H(T = 25°C) = 1.72 \times 10^{-5}\, atm^{-1}$
- Ethane: $H(T = 25°C) = 3.4 \times 10^{-5}\, atm^{-1}$
- Ethylene: $H(T = 25°C) = 8.53 \times 10^{-5}\, atm^{-1}$
- Helium: $H(T = 25°C) = 7 \times 10^{-6}\, atm^{-1}$
- Hydrogen: $H(T = 25°C) = 1.41 \times 10^{-5}\, atm^{-1}$
- Methane: $H(T = 25°C) = 2.55 \times 10^{-5}\, atm^{-1}$
- Nitrogen: $H(T = 25°C) = 1.18 \times 10^{-5}\, atm^{-1}$
- Oxygen: $H(T = 25°C) = 2.3 \times 10^{-5}\, atm^{-1}$

3. Calculate the mass concentration (in g/L) of oxygen and nitrogen dissolved in water from air (assume air is made by 21% in volume of oxygen and 79% in volume of nitrogen) at $25°C$ and atmospheric pressure. The molar masses of oxygen, nitrogen, and water are $31.998\ g/mol$, $28.013\ g/mol$, and $18.02\ g/mol$, respectively.

Assuming air as an ideal gas, the molar fractions equal the volume fractions.
The molar fractions of oxygen and nitrogen in air are $X_{O_2} = 0.21$ and $X_{N_2} = 0.79$, respectively and follow the relationship $X_{O_2} + X_{N_2} = 1$.

Applying Henry's law, the molar fraction of oxygen in water is:

$$\begin{aligned} x_{O_2}(T = 25°C) &= H_{O_2} p^*_{O_2} = H_{O_2} X_{O_2} p_{air} \\ &= 2.3 \times 10^{-5}\, atm^{-1} \times 0.21 \times 1\, atm = 4.83 \times 10^{-6} \end{aligned}$$

Remember that the molar fraction of a constituent i in a mixture is the ratio of its number of moles n_i over the total number of moles in the mixture (oxygen+nitrogen+water) $n = \sum_k n_k = n_{O_2} + n_{N_2} + n_{H_2O}$. It can be expressed as:

$$x_i = \frac{n_i}{n} = \frac{m_i}{M_i} \frac{1}{\sum_k \frac{m_k}{M_k}} = \frac{c_{m,i}}{M_i} \frac{1}{\sum_k \frac{c_{m,k}}{M_k}} = \frac{c_{m,i}}{M_i} \frac{\overline{M}}{\rho}$$

Where $c_{m,i}$ is the mass concentration of a constituent i, $\bar{M} = \rho / \sum_k \frac{c_{m,k}}{M_k}$ is the average molar mass of the mixture, and $\rho = \sum_k c_{m,k}$ is the density of the mixture.
Moreover, we have the relationship $\sum_k x_k = x_{O_2} + x_{N_2} + x_{H_2O} = 1$ for the molar fractions of the mixture.
Since $x_{H_2O} \approx 1$, we have $\rho \approx \rho_{H_20} = 1000\ g/L$ and $\bar{M} \approx M_{H_2O} = 18.02\ g/mol.$

The mass concentration of a constituent i in the mixture is therefore:

$$c_{m,i} = x_i \rho \frac{M_i}{\bar{M}} = x_i \rho_{H_2O} \frac{M_i}{M_{H_2O}}$$

Therefore, the mass concentration of oxygen in water is:

$$c_{m,O_2}(T = 25°C) = x_{O_2} \rho_{H_2O} \frac{M_{O_2}}{M_{H_2O}} = 4.83 \times 10^{-6} \times 1000 \times \frac{31.998}{18.02}$$
$$= 8.58 \times 10^{-3}\ g/L.$$

Applying Henry's law, the molar fraction of nitrogen in water is:

$$x_{N_2}(T = 25°C) = H_{N_2} p^*_{N_2} = H_{N_2} X_{N_2} p_{air}$$
$$= 1.18 \times 10^{-5}\ atm^{-1} \times 0.79 \times 1\ atm = 9.32 \times 10^{-6}$$

Therefore, the mass concentration of nitrogen in water is:

$$c_{m,N_2}(T = 25°C) = x_{N_2} \rho_{H_2O} \frac{M_{N_2}}{M_{H_2O}} = 9.32 \times 10^{-6} \times 1000 \times \frac{28.013}{18.02}$$
$$= 1.45 \times 10^{-2}\ g/L.$$

4. Calculate the mass concentration of dissolved air in water at $25°C$ exploiting the Henry's constant for air mixtures provided in Table 2, where H is given in atm^{-1}. The molar mass of gas mixtures is computed as follow:

$$\bar{M} = \sum_i X_i M_i$$

Where X_i is the molar fraction of the $i - th$ gas within the mixture, and M_i its molar mass. Compare the result with the mass concentration deduced from question 3.

The molar mass of air (oxygen+nitrogen) is:

$$\bar{M}_{air} = X_{O_2} M_{O_2} + X_{N_2} M_{N_2}$$

$$\bar{M}_{air} = 0.21 \times 31.998 + 0.79 \times 28.013 = 28.85\ g/mol.$$

Applying Henry's law, the molar fraction of air in water is:

$$x_{air}(T = 25°C) = H_{air} p^*_{air} = 1.4 \times 10^{-5} atm^{-1} \times 1 atm = 1.4 \times 10^{-5}$$

Therefore, the mass concentration of air in water is:

$$c_{m,air}(T = 25°C) = x_{air} \rho_{H_2O} \frac{\overline{M}_{air}}{M_{H_2O}} = 1.4 \times 10^{-5} \times 1000 \times \frac{28.85}{18.02}$$
$$= 2.24 \times 10^{-2}\ g/L.$$

Adding up the results from question 3 gives:

$$c_{m,air}(T = 25°C) = c_{m,O_2}(T = 25°C) + c_{m,N_2}(T = 25°C) = 2.3 \times 10^{-2} g/L$$

5. Does the O_2/N_2 ratio is conserved when air is dissolved in water?

The O_2/N_2 molar ratio <u>in air</u> is:

$$\frac{X_{O_2}}{X_{N_2}} = \frac{0.21}{0.79} = 0.27$$

The O_2/N_2 molar ratio <u>in water</u> is:

$$\frac{x_{O_2}}{x_{N_2}} = \frac{4.83 \times 10^{-6}}{9.32 \times 10^{-6}} = 0.52$$

The molar ratio is <u>not conserved</u>. In terms of molar fractions, a higher amount of oxygen is present in water than in air with respect to nitrogen.