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H₂O₂ Conversions

FORMULAS AND METHODS
FOR CALCULATING VAPORIZED
HYDROGEN PEROXIDE PARAMETERS

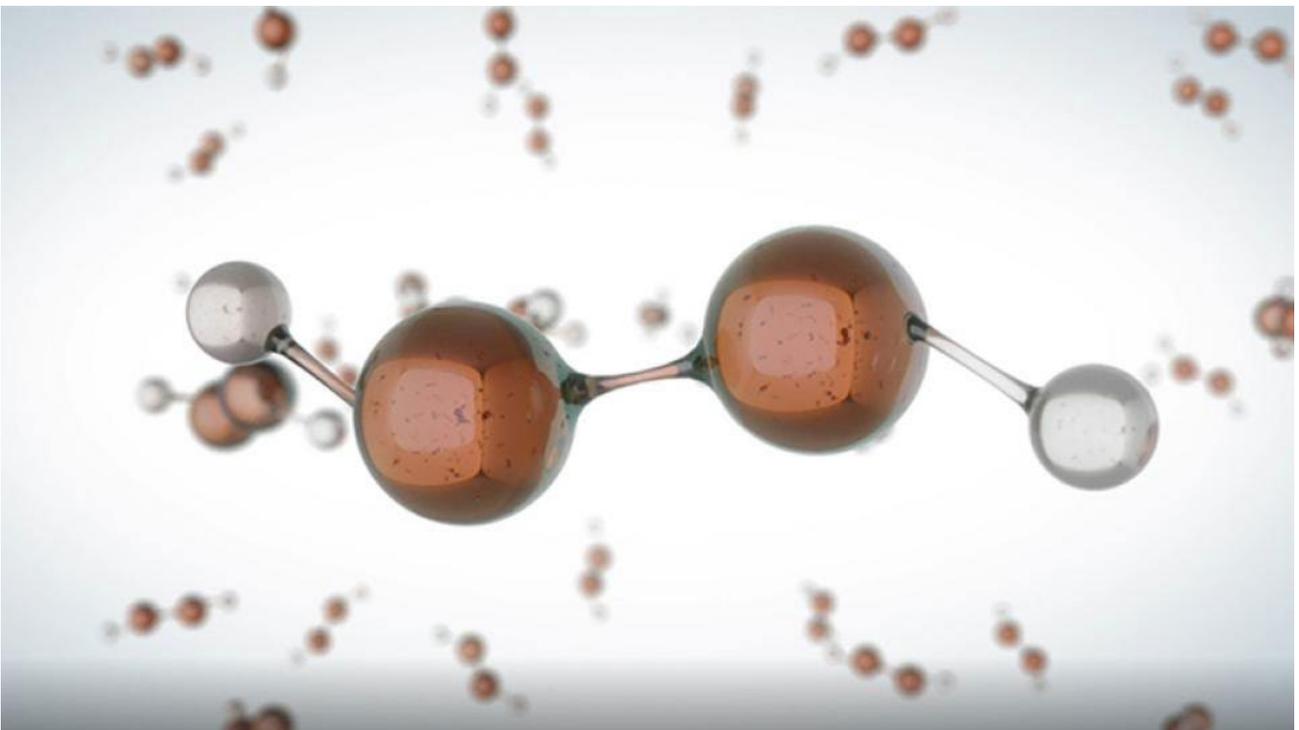


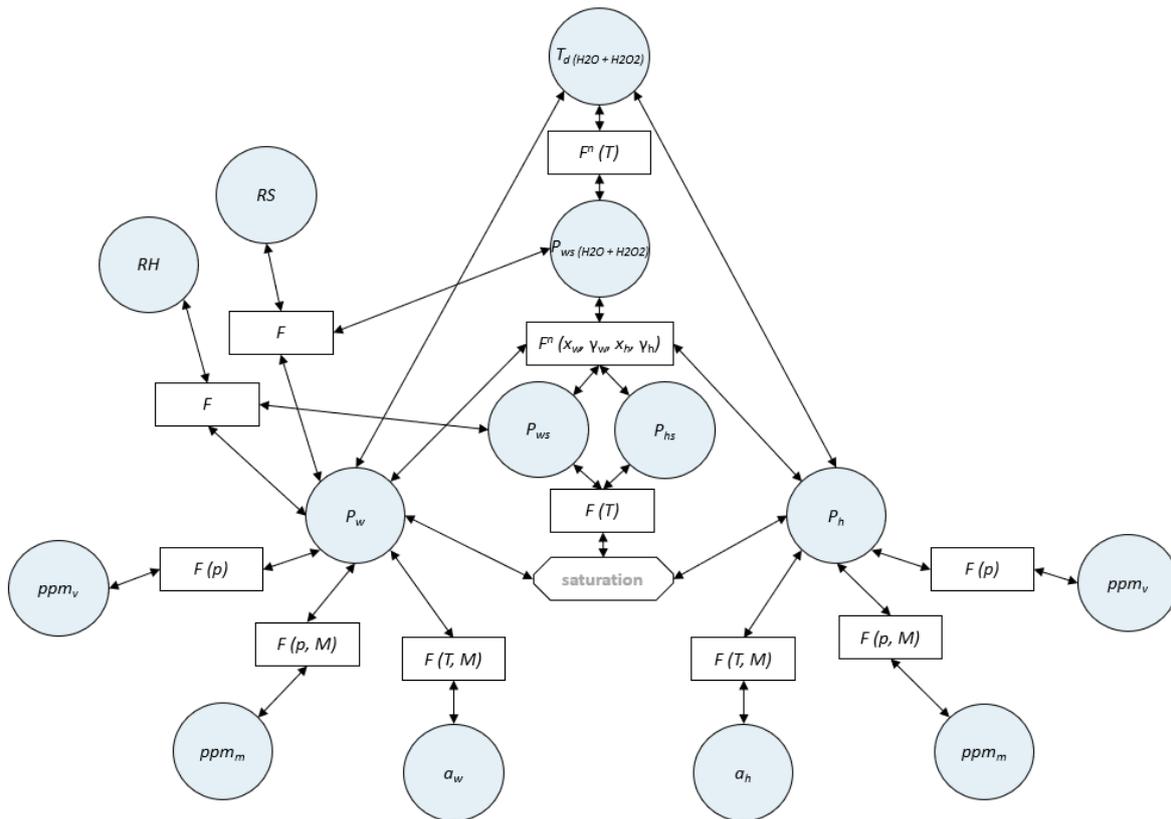
Table of contents

1. Foreword.....	2
2. Water and H ₂ O ₂ content - ppm (parts per million).....	3
2.1 ppm_v - volume/volume.....	3
2.2 ppm_m - mass/mass.....	3
3. Relative humidity - RH	4
4. Relative saturation - RS	4
5. Water vapor saturation pressure - P_{ws}	5
6. H ₂ O ₂ vapor saturation pressure - P_{hs}	6
7. Water vapor saturation pressure in an H ₂ O ₂ environment - $P_{ws}(H_2O + H_2O_2)$	7
7.1 Raoult's law for vapor pressure.....	7
7.2 Activity coefficient of water and H ₂ O ₂	7
7.3 Mole fraction of water and H ₂ O ₂	8
7.4 Iterative calculation for $P_{ws}(H_2O + H_2O_2)$	8
8. Dew point in an H ₂ O ₂ environment - $T_d(H_2O + H_2O_2)$	10
8.1 Dew point to vapor pressure - $T_d(H_2O + H_2O_2)$ to P_w and P_h	10
8.2 Vapor pressure to dew point - P_w and P_h to $T_d(H_2O + H_2O_2)$	10
9. Absolute concentration of water and H ₂ O ₂ - a_w and a_h	12
10. Molecular weight	13
11. Conversions to Imperial units and non-SI units	14
12. References.....	14

H₂O₂ conversions

1. Foreword

This document describes the functions and methods for calculating different humidity and vaporized hydrogen peroxide variables. For information on measuring liquid hydrogen peroxide please see our Web page on [Chemical Processing](#). As shown in the diagram below, the partial vapor pressure (P_w/P_h) and saturation vapor pressure (P_{ws}/P_{hs}) are the key factors in parametric calculations. Other parameters can be derived from these parameters by using functions, iterative methods, and auxiliary parameters: temperature and pressure. The units selected for this document are in accordance with the International System of Units (SI). Conversion to Imperial units can be found from chapter 11.



- P_{ws} = Saturation vapor pressure over water in Pa
- P_{hs} = Saturation vapor pressure over hydrogen peroxide in Pa
- $P_{ws}(H_2O+H_2O_2)$ = Saturation vapor pressure over water in H₂O₂ environments in Pa
- P_w/P_h = Vapor saturation pressure over water / hydrogen peroxide in Pa
- RH = Relative humidity in %rh
- RS = Relative saturation in %rs
- $T_d(H_2O+H_2O_2)$ = Dew Point in °C
- a_w = Absolute humidity in g/m³
- a_h = Absolute hydrogen peroxide in mg/m³
- ppm_v = Parts per million (volume_{H₂O₂ or H₂O}/volume_{gas})
- ppm_m = Parts per million (mass_{H₂O}/mass_{gas})
- $F(T, p, M)$ = Function with auxiliary quantities: temperature, pressure, or molar
- $F^n(T, p)$ = Iterative method with auxiliary quantities: temperature and pressure

2. Water and H₂O₂ content – ppm (parts per million)

Parts per million is a unitless parameter typically used to state a small amount of chemical concentration. There are two different ways to express H₂O and H₂O₂ contents and care should be taken in this because, in both chemicals, contents may refer to either mass fraction or volume fraction. We describe differences in these expressions in the following chapters.

2.1 ppm_v – volume/volume

$$ppm_V = \frac{P_x}{p} \cdot 10^6, \text{ where} \quad (\text{Equation 1})$$

P_x = Vapor pressure of chemical X in Pa

p = Total pressure in Pa

Examples:

To calculate water vapor concentration in volume fraction (ppm_v) in the following condition:

P_w = 982.26 Pa

p = 101325 Pa

$$ppm_{V\ H_2O} = \frac{P_w}{p} \cdot 10^6 = \frac{982.26\ \text{Pa}}{101325\ \text{Pa}} \cdot 10^6 = 9694\ \text{ppm}_v$$

To calculate H₂O₂ vapor concentration in volume fraction (ppm_v) in following condition:

P_h = 50.66 Pa

p = 101325 Pa

$$ppm_{V\ H_2O_2} = \frac{P_h}{p} \cdot 10^6 = \frac{50.66\ \text{Pa}}{101325\ \text{Pa}} \cdot 10^6 = 500\ \text{ppm}_v$$

2.2 ppm_m – mass/mass

$$ppm_m = \frac{M_x \cdot P_x}{M_{gas} \cdot p} \cdot 10^6, \text{ where} \quad (\text{Equation 2})$$

M_x = Molecular weight of chemical X in g·mol⁻¹ (H₂O₂ = 34.0136 g·mol⁻¹)¹

M_{gas} = Molecular weight of dry gas in g·mol⁻¹ (air = 28.965)¹

Example:

To calculate H₂O₂ concentration in mass fraction (ppm_m) in following condition:

$M_{H_2O_2}$ = 34.0136 g·mol⁻¹

P_h = 50.66 Pa

p = 101325 Pa

$$ppm_{m\ H_2O_2} = \frac{34.0136\ \text{g}\cdot\text{mol}^{-1} \cdot 50.66\ \text{Pa}}{28.965\ \text{g}\cdot\text{mol}^{-1} \cdot 101325\ \text{Pa}} \cdot 10^6 = 587\ \text{ppm}_m$$

¹See chapter 10 Molecular weight

3. Relative humidity – RH

Relative humidity indicates the humidity value derived from water vapor only. Relative humidity is defined at all temperatures and pressures as the ratio of the water vapor pressure (P_w) to the saturation water vapor pressure over water (P_{ws}) at the gas temperature:

$$RH = \frac{P_w}{P_{ws}} \cdot 100 \%rh \quad (\text{Equation 3})$$

The total pressure does not enter the definition. Above 100°C the same definition is valid. But as the saturation vapor pressure P_{ws} is greater than 1,013 hPa (normal ambient pressure), the RH cannot reach 100% in an unpressurized system. This definition is also valid below 0°C. Here 100% rh is impossible because condensation will occur at a lower humidity than 100% (when the vapor is saturated against ice).

4. Relative saturation – RS

Relative saturation indicates the humidity value derived from the combination of water vapor and hydrogen peroxide vapor. Relative saturation is defined at all temperatures and pressures as the ratio of the water vapor pressure (P_w) to the saturation water vapor pressure at a given H_2O_2 vapor concentration ($P_{ws}(H_2O + H_2O_2)$) at the gas temperature:

$$RS = \frac{P_w}{P_{ws}(H_2O+H_2O_2)} \cdot 100 \%rs \quad (\text{Equation 4})$$

Example:

To calculate RS in the following condition:

$$ppm_v H_2O_2 = 500 ppm_v$$

$$T = 20 \text{ }^\circ\text{C} \Rightarrow T_k = 293.15 \text{ K}$$

$$RH = 42.0 \%rh$$

$$p = 101325 \text{ Pa}$$

$$P_{ws}(H_2O + H_2O_2) (17) = 1068.85 \text{ Pa}$$

$$P_w(3) = 982.26 \text{ Pa}$$

Answer: $RS = 92.50 \%rs$

5. Water vapor saturation pressure - P_{ws}

Water vapor saturation pressure indicates the maximum vapor pressure of pure water at a given temperature. At saturation vapor pressure, water is in thermodynamic equilibrium, meaning that its liquid and solid phases are in equilibrium. Many saturation vapor pressure equations exist to calculate the saturation pressure of water vapor over a surface of liquid water (P_{ws}). Water vapor saturation pressure can be calculated using Sonntag's equation [1]. This equation is valid in temperature ranges from 0 °C to 100 °C.

$$P_{ws}(T_K) = a_0 \cdot \exp\left[\frac{a_1}{T_K} + a_2 + a_3T + a_4T^2 + a_5 \ln(a_6 \cdot T_K)\right], \text{ where} \quad (\text{Equation 5})$$

P_{ws} = Saturation vapor pressure above water in Pa

T_K = Temperature in K

Table 1: Numerical values for coefficients $a_0 \dots a_6$

Coefficients a_n	Above water (P_{ws}) (0 to 100 °C)
a_0	1 [Pa]
a_1	-6.0969385E+03 [K]
a_2	2.12409642E+01
a_3	-2.711193E-02 [K ⁻¹]
a_4	1.673952E-05 [K ⁻²]
a_5	2.433502
a_6	1 [K ⁻¹]

Example:

To calculate water vapor saturation pressure in 20 °C temperature:

$$T = 20 \text{ °C} \Rightarrow T_K = 20 + 273.15 = 293.15 \text{ K}$$

$$P_{ws} = 2339.25 \text{ Pa}$$

6. H₂O₂ vapor saturation pressure - P_{hs}

Hydrogen peroxide vapor saturation pressure indicates the maximum vapor pressure of pure H₂O₂ vapor at a given temperature. At saturation vapor pressure, hydrogen peroxide is in thermodynamic equilibrium, meaning that its liquid and gas phases are in equilibrium. The following equation by Scatchard et. al. can be used to calculate the saturation pressure of H₂O₂ vapor over a surface of liquid H₂O₂ (P_{hs}) [2].

$$P_{hs}(T_K) = \frac{10^{[a_0 + \frac{a_1}{T} + a_2 \cdot \log T + a_3 \cdot T]}}{7.5006 \cdot 10^{-3}}, \text{ where} \quad (\text{Equation 6})$$

P_{hs} = Saturation vapor pressure above H₂O₂ in Pa

T_K = Temperature in K

Table 2: Numerical values for coefficients $a_0 \dots a_3$

Coefficients a_n	Above H ₂ O ₂ (P_{hs})
a_0	44.576 [Pa]
a_1	-4025 [K]
a_2	-12.996 [K ⁻¹]
a_3	0.004605 [K ⁻¹]

Example:

To calculate the H₂O₂ vapor saturation pressure in 20 °C temperature:

$$T = 20 \text{ °C} \Rightarrow T_K = 20 + 273.15 = 293.15 \text{ K}$$

$$P_{hs} = 181.30 \text{ Pa}$$

7. Water vapor saturation pressure in an H₂O₂ environment – $P_{ws}(H_2O + H_2O_2)$

Water vapor saturation pressure $P_{ws}(H_2O + H_2O_2)$ in an environment that contains H₂O₂ vapor indicates the maximum water vapor pressure when hydrogen peroxide vapor is present. Calculating water vapor saturation pressure in an H₂O₂ environment involves complex equations because the saturation point depends on hydrogen peroxide and water vapor concentrations, as well as temperature. To calculate water vapor saturations in these environments, we can derive the equation, $P_{ws}(H_2O + H_2O_2)$, from Raoult's law. The equation is then solved through an iterative procedure.

7.1 Raoult's law for vapor pressure

Raoult's law for non-ideal vapor pressures states that partial pressure of each chemical X (P_x) in a solution can be calculated:

$$P_x = \gamma_x \cdot x_x \cdot P_{xs}, \text{ where} \quad (\text{Equation 7})$$

- P_x = Vapor pressure of chemical X in Pa
- γ_x = Activity coefficient of chemical X
- x_x = Mole fraction of chemical X
- P_{xs} = Saturation vapor pressure above chemical X in Pa

Therefore, we can form similar equations for water and hydrogen peroxide respectively:

$$P_w = \gamma_w \cdot x_w \cdot P_{ws} \text{ and } P_h = \gamma_h \cdot x_h \cdot P_{hs}, \text{ where} \quad (\text{Equation 8,9})$$

- P_w = Vapor pressure of water in Pa
- P_h = Vapor pressure of H₂O₂ in Pa
- γ_w = Activity coefficient of water
- γ_h = Activity coefficient of H₂O₂
- x_w = Mole fraction of water
- x_h = Mole fraction of H₂O₂
- P_{ws} = Saturation vapor pressure above water in Pa
- P_{hs} = Saturation vapor pressure above H₂O₂ in Pa

7.2 Activity coefficient of water and H₂O₂

Hydrogen peroxide and water interact with each other in a vapor mixture; therefore the mixture will not comply with an ideal solution model. To account for the deviation from ideal behavior, we use activity coefficients. The activity coefficients γ_w (for H₂O) and γ_h (for H₂O₂) can be calculated with the following formulas by Scatchard et. al. [2]:

$$\gamma_w = \exp\left\{\frac{(1-x_w)^2}{RT} \cdot [B_0 + B_1(1 - 4x_w) + B_2(1 - 2x_w) \cdot (1 - 6x_w)]\right\} \text{ and} \quad (\text{Equation 10})$$

$$\gamma_h = \exp\left\{\frac{x_w^2}{RT} \cdot [B_0 + B_1(3 - 4x_w) + B_2(1 - 2x_w) \cdot (5 - 6x_w)]\right\}, \text{ where} \quad (\text{Equation 11})$$

R = Universal gas constant 1.986 cal·K⁻¹·mol⁻¹

Table 3: Numerical values for coefficients $B_0 \dots B_2$

Coefficients B_n	For water + H ₂ O ₂ solution
B_0	-752 + 0.97·T [cal·mol ⁻¹]
B_1	85 [cal·mol ⁻¹]
B_2	13 [cal·mol ⁻¹]

7.3 Mole fraction of water and H₂O₂

Raoult's law states that in a chemical mixture, the sum of mole fractions of all mixture components must be equal to one. Therefore, in the case of a mixture containing both water and H₂O₂:

$$x_h + x_w = 1 \quad (\text{Equation 12})$$

In liquid solutions, the mole fraction of H₂O₂ (x_h) can be calculated as a fraction amount of a substance:

$$x_h = \frac{n_h}{n_h + n_w}, \text{ where} \quad (\text{Equation 13})$$

n_h = Amount of substance for H₂O₂ in mol

n_w = Amount of substance for water in mol

The amount of H₂O₂ can be calculated using the equation below. A similar equation can also be used for calculating the amount of H₂O.

$$n_h = \frac{w\%_{H_2O_2}}{M_{H_2O_2}}, \text{ where} \quad (\text{Equation 14})$$

$w\%_{H_2O_2}$ = H₂O₂ liquid concentration in mass percent

$M_{H_2O_2}$ = Molecular weight of chemical H₂O₂ in g·mol⁻¹

In vapor mixtures of H₂O and H₂O₂, mole fractions behave differently compared to liquids. In the case of vaporized mixtures, mole fraction cannot be calculated using equations 13 and 14, which apply to liquids. At condensation, when the vapor starts to saturate i.e.: form droplets, the mole fraction can be different depending on the temperature, water, and H₂O₂ concentrations. Therefore, the mole fraction in the vapor phase must be determined using an iterative procedure.

7.4 Iterative calculation for $P_{ws} (H_2O + H_2O_2)$

In order to calculate water vapor saturation pressure $P_{ws} (H_2O + H_2O_2)$ in an H₂O₂ vapor environment, we need to find mole fractions from equations 8 and 9:

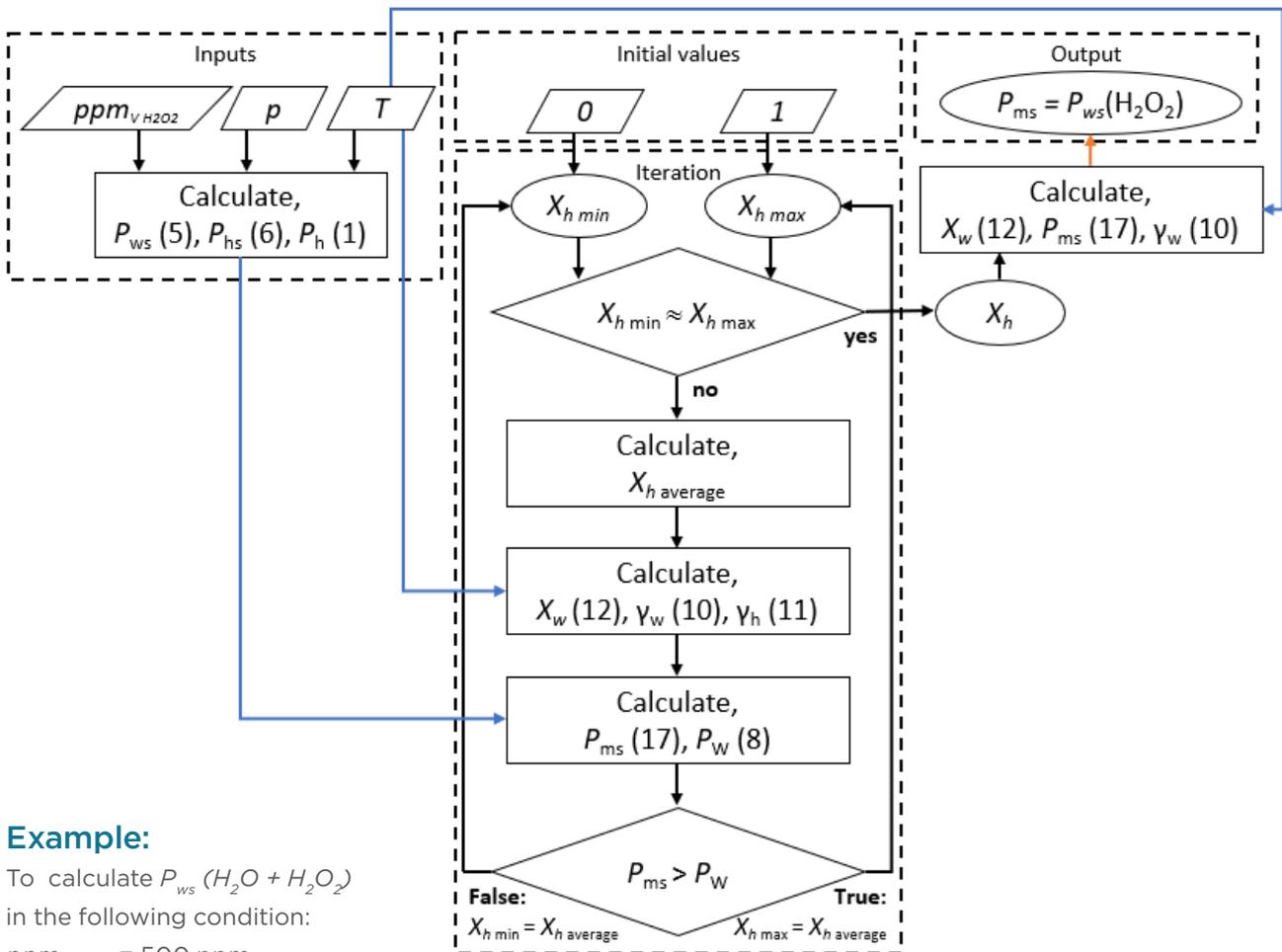
$$x_w = \frac{P_w}{\gamma_w P_{ws}} \text{ and } x_h = \frac{P_h}{\gamma_h P_{hs}} \quad (\text{Equations 15, 16})$$

We then combine equations 15 and 16 with equation 12 to find water vapor pressure (P_w):

$$P_w = \gamma_w P_{ws} \left(1 - \frac{P_h}{\gamma_h P_{hs}} \right) \xrightarrow{\text{rename}} P_{ms} \quad (\text{Equation 17})$$

To be unambiguous, let us rename this water vapor pressure as "mixture water vapor pressure" (P_{ms}).

There are now two equations presented for water vapor pressure (equations 8, 17) and one unknown variable (mole fraction of water x_w). Both equations 8 and 17 should produce the same value for water vapor pressure. The Mole fraction of water can be solved by using an iterative procedure shown in the flow diagram below. By using iterated mole fraction x_h , water vapor can be calculated using equation 17 or 8. The calculated water vapor pressure indicates the water vapor saturation pressure in a vaporized H₂O₂ environment, $P_{ws} (H_2O + H_2O_2)$. A similar calculation is presented by Parks et al [3].



Example:

To calculate $P_{ws}(H_2O + H_2O_2)$ in the following condition:

- $ppm_{V_{H_2O_2}} = 500\ ppm_v$
- $T = 20\ ^\circ C \Rightarrow T_k = 293.15\ K$
- $p = 101325\ Pa$
- $P_{ws}(5) = 2339.25\ Pa$
- $P_{hs}(6) = 181.30\ Pa$
- $P_h(1) = 50.66\ Pa$

Iteration					
Step	$X_{h\ min}\ ^\circ C$	$X_{h\ max}\ ^\circ C$	$X_{h\ average}\ ^\circ C$	$P_w\ Pa$	$P_{ms}\ Pa$
1	0 [initial]	1 [initial]	0.50	1038.89	823.27
2	0	0.5	0.25	917.34	1596.25
3	0.25	0.5	0.375	1056.50	1190.28
4	0.375	0.5	0.438	1062.04	999.89
5	0.375	0.438	0.406	1063.45	1093.57
6	0.406	0.438	0.422	1063.71	1046.32
7	0.406	0.422	0.414	1063.83	1069.85
8	0.414	0.422	0.418	1063.83	1058.06
..
19	0.416	0.416	0.416	1063.85	1063.85
20	0.416	0.416	0.416	1063.85	1063.85

Answer: $P_{ms} = P_{ws}(H_2O + H_2O_2) = 1068.85\ Pa$

8. Dew point in an H_2O_2 environment - $T_d (H_2O + H_2O_2)$

The dew point temperature (T_d) is the temperature to which air must be cooled to become saturated with water vapor. The term T_d is valid when dew point temperature is equal to or above 0 °C. When H_2O_2 vapor is present in the air mixture, deriving the dew point from only the water vapor is insufficient because the H_2O_2 vapor will change the dew point. This is because H_2O_2 vapor effects the water vapor saturation pressure, $P_{ws} (H_2O + H_2O_2)$; with an increase in H_2O_2 vapor, the water vapor saturation pressure will decrease. In other words, when the H_2O_2 vapor concentration is increased, the maximum amount of water vapor that the air can hold decreases. In order to distinguish dew point derived from only water (T_d), let's abbreviate this mixture dew point $T_d (H_2O + H_2O_2)$ which indicates the dew point temperature in an H_2O_2 vapor environment.

8.1 Dew point to vapor pressure - $T_d (H_2O + H_2O_2)$ to P_w and P_h

Calculating the vapor pressure from $T_d (H_2O + H_2O_2)$ is a straightforward operation. For water vapor pressure, use equation 8 to calculate the water vapor saturation pressure, mole fraction and activity coefficient in $T_d (H_2O + H_2O_2)$ condition:

$$P_w(T_K) = \gamma_w(T_d + 273.15) \cdot x_w(T_d + 273.15) \cdot P_{ws}(T_d + 273.15) \quad (\text{Equation 18})$$

For H_2O_2 vapor pressure, use equation 9 to calculate the H_2O_2 vapor saturation pressure, mole fraction and activity coefficient in $T_d (H_2O + H_2O_2)$ condition:

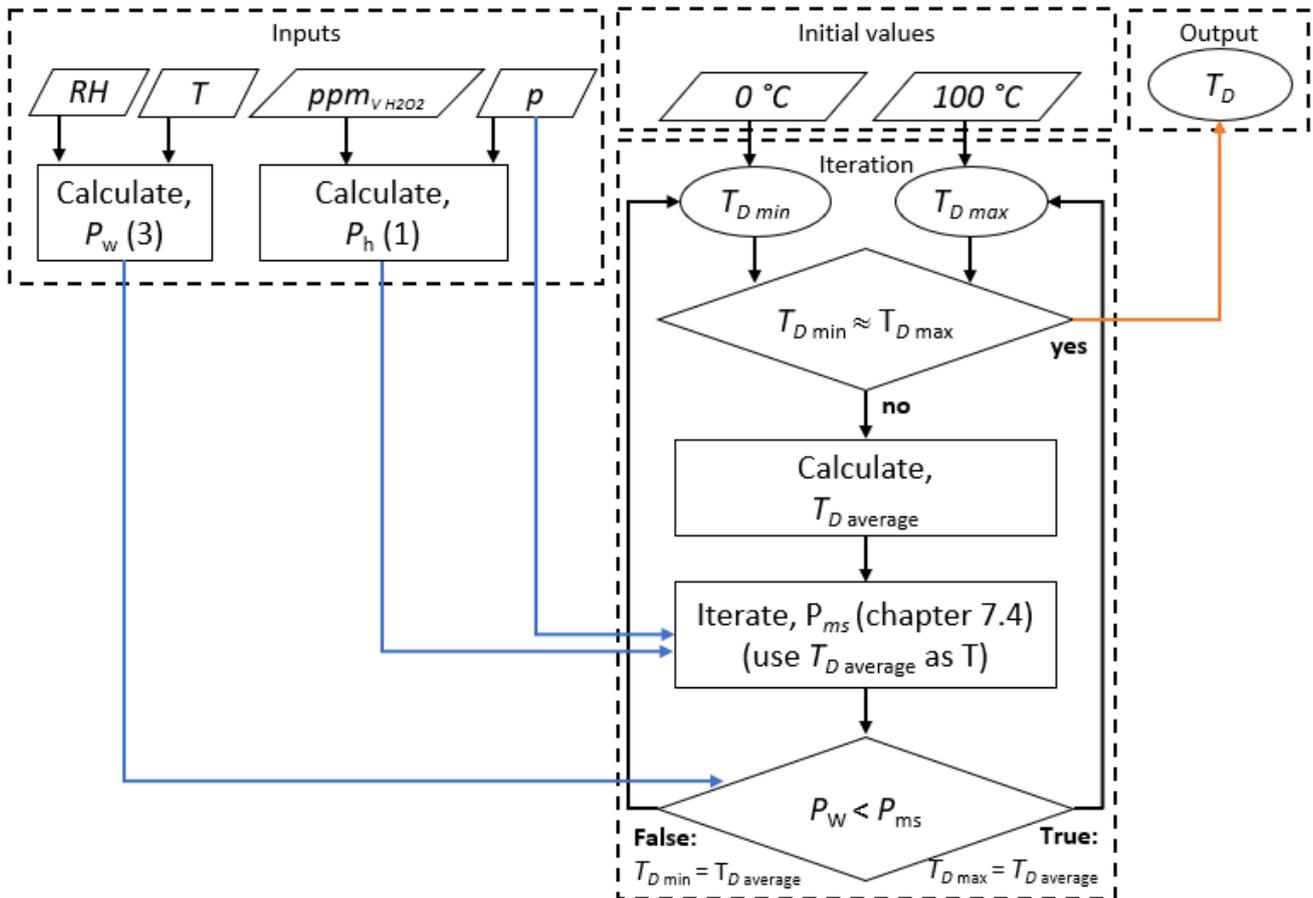
$$P_h(T_K) = \gamma_h(T_d + 273.15) \cdot x_h(T_d + 273.15) \cdot P_{hs}(T_d + 273.15) \quad (\text{Equation 19})$$

When $\text{ppm}_{H_2O_2} = 0 \text{ ppm}_v$, then $Y_w = 1$, $X_w = 1$ and $x_h = 0$ and both equation above simplify. Therefore, at that point $T_d = T_d (H_2O + H_2O_2)$.

8.2 Vapor pressure to dew point - P_w and P_h to $T_d (H_2O + H_2O_2)$

Calculating dew point from vapor pressure, temperature, and pressure involves complex equations, because the mole fraction, activity coefficient, and vapor pressure are dependent on the dew point result. Dew point can be solved by using an iterative procedure.

Initial values for a trial-and-error process should be wide enough to accommodate the result within its boundaries. Proper values for the majority of applications are between 0 °C ... 100 °C. The vapor pressure to dew point iterative process is shown in the flow diagram below:



Example:

To calculate $T_d(H_2O + H_2O_2)$ in following condition:

$$ppm_{v H_2O_2} = 500\text{ ppm}_v$$

$$T = 20\text{ }^\circ\text{C} \Rightarrow T_k = 293.15\text{ K}$$

$$RH = 42.0\text{ \%rh}$$

$$p = 101325\text{ Pa}$$

$$P_w(1) = 982.26\text{ Pa}$$

$$\text{Answer: } T_d(H_2O + H_2O_2) = 19.35\text{ }^\circ\text{C}$$

9. Absolute concentration of water and H₂O₂ – a_w and a_h

Absolute concentration of water – also called absolute humidity – is defined as the mass of water vapor in a certain volume. In the case of H₂O₂, absolute hydrogen peroxide is defined as the mass of H₂O₂ vapor in a certain volume. If ideal gas behavior is assumed, the absolute concentration can be calculated using:

$$a_x = \frac{M_x \cdot P_x}{R \cdot T_K}, \text{ where} \quad (\text{Equation 20})$$

- a_x = Absolute concentration of chemical X in g·m⁻³
- M_x = Molecular mass of chemical X in g·mol⁻¹
- R = Universal gas constant 8.3145 J·K⁻¹·mol⁻¹
- P_x = Vapor pressure of chemical X in Pa
- T_K = Temperature in K

Example:

To calculate absolute humidity in following condition:

$$RH = 42.0 \%rh$$

$$T = 20 \text{ }^\circ\text{C} \Rightarrow T_K = 293.15 \text{ K}$$

$$\rho = 101325 \text{ Pa}$$

$$M_{H_2O} = 18.0146 \text{ g}\cdot\text{mol}^{-1}$$

$$P_{ws}(5) = 2339.25 \text{ Pa}$$

$$P_w(1) = 982.26 \text{ Pa}$$

$$a_w = \frac{M_{H_2O} \cdot P_w}{R \cdot T_K} = \frac{18.0146 \text{ g}\cdot\text{mol}^{-1} \cdot 982.26 \text{ Pa}}{8.3145 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1} \cdot 293.15 \text{ K}} = 7.3 \text{ g}\cdot\text{m}^{-3}$$

To calculate absolute H₂O₂ in following condition:

$$\rho pm_{V_{H_2O_2}} = 500 \text{ ppm}_v$$

$$T = 20 \text{ }^\circ\text{C} \Rightarrow T_K = 293.15 \text{ K}$$

$$\rho = 101325 \text{ Pa}$$

$$M_{H_2O_2} = 34.0136 \text{ g}\cdot\text{mol}^{-1}$$

$$P_h(1) = 50.66 \text{ Pa}$$

$$a_h = \frac{M_{H_2O_2} \cdot P_h}{R \cdot T_K} = \frac{34.0136 \text{ g}\cdot\text{mol}^{-1} \cdot 50.66 \text{ Pa}}{8.3145 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1} \cdot 293.15 \text{ K}} = 0.70699 \text{ g}\cdot\text{m}^{-3} = 707.0 \text{ mg}\cdot\text{m}^{-3}$$

¹See chapter 10 Molecular weight

10. Molecular weight

The molecular weight (molar mass M) of a substance is needed in mass-based calculations, such as absolute concentrations and ppm concentration in mass fraction. Molecular mass of a substance is the sum of the mole fractions of its gas components multiplied by their molar mass. See "Atomic weights of the elements 2013" by J. Meija et al. [4]. Let us take dry air as an example. There are seasonal variations in the composition of the air as well as a continuous change, especially in the CO_2 content. Here is a 4-component simplification of dry air:

Component	Molar ratio ($\text{mol}\cdot\text{mol}_{\text{air}}^{-1}$)	Molar mass ($\text{g}\cdot\text{mol}^{-1}$)	Molar mass in air ($\text{g}\cdot\text{mol}_{\text{air}}^{-1}$)
N_2	0.7808	28.013	21.872
O_2	0.2095	31.999	6.7037
Ar	0.0093	39.948	0.3715
CO_2	0.0004	44.01	0.0176
Total	1		28.965

The molar mass of air is $28.965 \text{ g}\cdot\text{mol}^{-1}$.

Other gas mixtures can be calculated by using a similar method.

The chemical formula of water is H_2O , which means that each molecule contains one oxygen and two hydrogen atoms. Similarly, the chemical formula of hydrogen peroxide is H_2O_2 , which means that each molecule contains two oxygen and two hydrogen atoms.

Component	Molar mass (g/mol^{-1})
H	1.0078
O	15.999
$M_{\text{H}_2\text{O}}$	18.0146
$M_{\text{H}_2\text{O}_2}$	34.0136

The molar mass of water is $18.0146 \text{ g}\cdot\text{mol}^{-1}$ and molar mass of hydrogen peroxide is $34.0136 \text{ g}\cdot\text{mol}^{-1}$.

11. Conversions to Imperial units and non-SI units

- Fahrenheit temperature: $T_{\circ F} = T_{\circ C} \cdot \frac{9}{5} + 32$
- psi (pounds per square inch): $p_{psi} = 6894.76 \cdot p_{Pa}$
- Absolute concentration in grains per cubic feet: $A_{gr/ft^3} = 2.2883 \cdot A_{g/kg}$
- Conversion from ppm_v to milliliters per cubic meter: $1 \text{ ppm}_v = 1 \frac{mL}{m^3}$

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