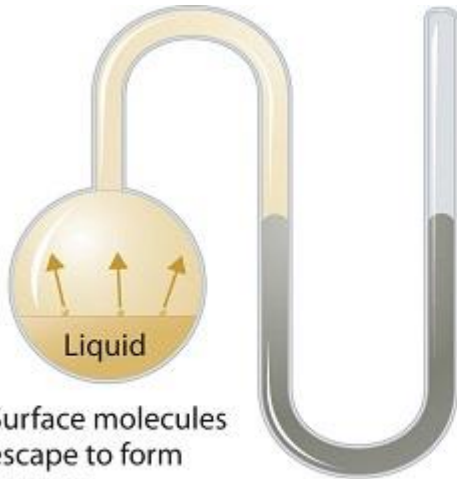




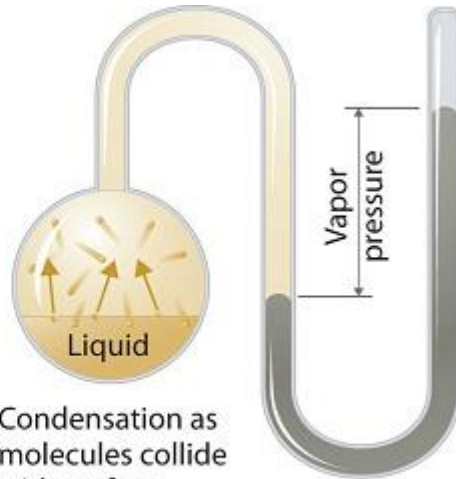
GENERAL CONCEPTS AND FUNDAMENTALS (II)

Vapor pressure VS partial pressure



Surface molecules escape to form a vapor

(a)



Condensation as molecules collide with surface

(b)

Vapor Pressure

It is exerted by liquid or solid vapor on its condensed phase in equilibrium

Well explained by Raoult's Law

Applicable in solid and liquid phases

Independent of the surface area or the volume of the system

Calculated using the mole fraction of the solute

Partial Pressure

It is exerted by individual gases in a non-reactive gas mixture

Well explained by Dalton's Law

Applicable in gaseous phases only

Calculated using the gases in the same volume

Calculated using the mole fraction of the gas

Vapour pressure is the pressure exerted by the vapor in its thermodynamic equilibrium on its liquid or solid state at a given temperature in a closed system when both the vapor and the liquid (solid) are in contact. The vapor pressure can also occur in ideal mixtures as explained by the **Raoult's Law**. It states that the **partial vapor pressure** of a particular component in a liquid or solid mixture is equal to the vapor pressure of that component multiplied by its mole fraction in that mixture at a given temperature.

The idea of **partial pressure** was first proposed by the renowned scientist John Dalton. It gave birth to his Law of Partial Pressures which states that the total pressure exerted by **an ideal mixture of gases** is equal to the sum of the partial pressures of individual gases. The partial pressure of any gas in that mixture is calculated by multiplying the total pressure by the molar fraction of the individual gas.

Gaseous Pollutants: GASES and VAPORS

Gas

Vapor

Common properties

- Both are in the **gaseous** state of matter;
- Both gas and vapour particles are widely separated, freely moving molecules;
- Both **will expand** to fill the container in which are kept;
- Both exert pressure in **all** direction.

At room T and given P

Refers to a substance that has a **single** defined thermodynamic state

Refers to a substance that is a **mixture of two phases**, namely gaseous and liquid phase. A vapour is a gas state of a substance at a T where it can co-exist with its liquid or solid state

→ for a liquid or solid to become gas it have to overcome the boiling / sublimation points, resp.

A “true” gas is far from the liquid state → the T of the substance is above its critical point (the highest T at which it can be condensed)

→ for a liquid or solid to become vapor it does not have to first boil.

A vapour is a substance in the gaseous state that is not far from being a liquid. → It can exist below its dew point.

SO₂

NO₂

NO

CO

H₂O

VOC

Gas mixture – Dalton's law

Dalton's law (partial pressures)

$$p = \sum_i p_i$$

- p = total pressure
- p_i = partial pressure of "i" = pressure exerted by "i" if occupying **alone** the same **total volume V** of the mixture at the same T
- ideal gases

$$\frac{p_i}{p} = \frac{\frac{n_i \cdot RT}{V_T}}{\frac{n_T \cdot RT}{V_T}} = \frac{n_i}{n_T} = y_i$$

$$p_i = y_i \cdot p$$

y_i = mole fraction of "i"

Amagat's law (partial volumes)

$$V_i = y_i \cdot V$$

- V_i = partial volume of "i" = volume occupied by "i" **alone** at the **total pressure P** of the mixture at the same T

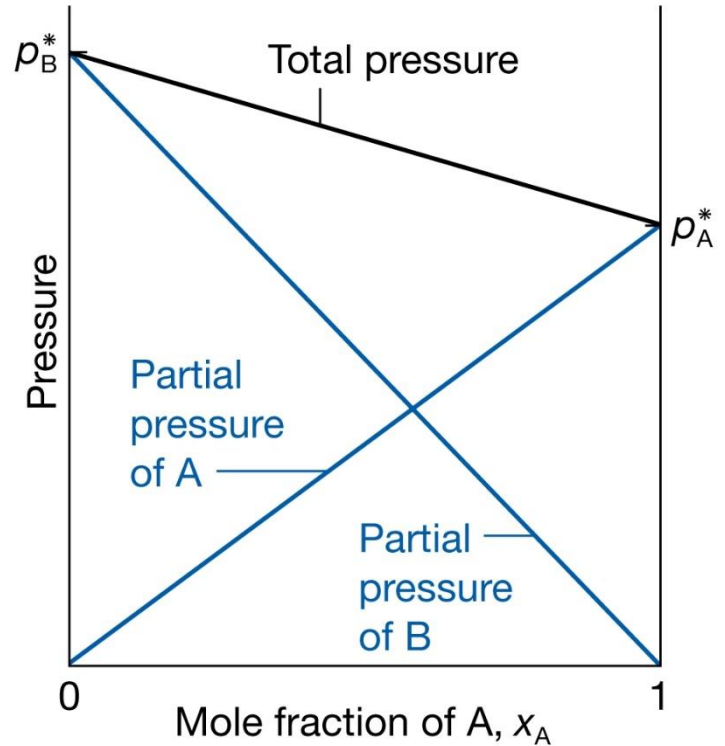
Vapor pressure of solvents – Raoult's law

Raoult's law for a single component in an ideal solution is stated as:

$$p_i = p_i^\circ \cdot x_i$$

where

- p_i is the partial vapour pressure of the component «i» in the gaseous mixture (above the solution);
- p_i° is the vapour pressure of the pure component «i»;
- x_i is the mole fraction of the component «i» in the mixture (in the solution).



Example of a mixture of two components. Each component contributes its own partial pressure to the solution vapour pressure

Vapor pressure of solvents – Henry's law

Henry law is valid for non reactive gases. What does means for reactive gas as SO₂?

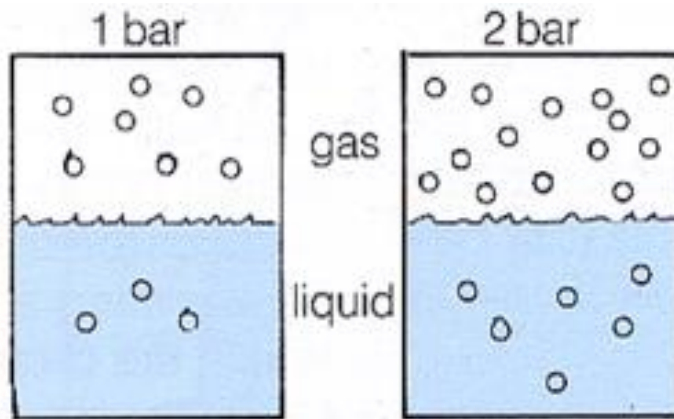
The statement of Henry's law is:

$$p_i = x_i \cdot k_{H,i}$$

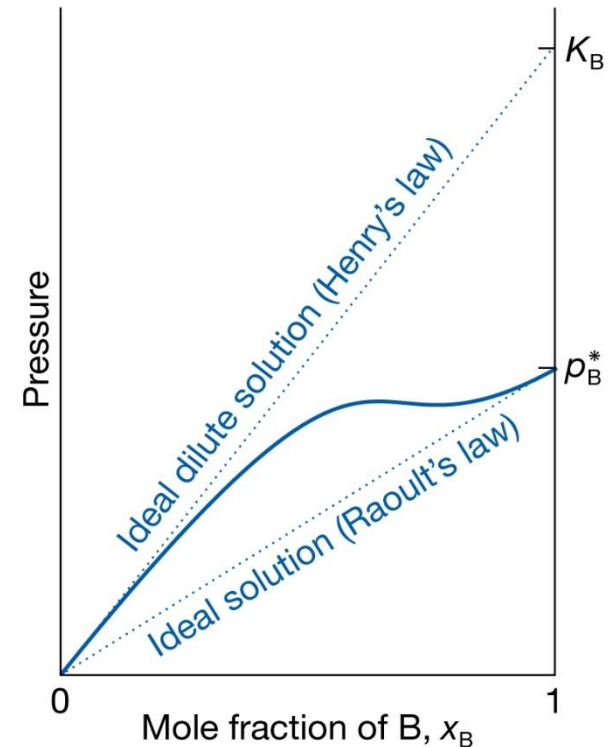
It looks like Raoult's law except that you have this constant $k_{H,i}$ instead of p_i° (the vapor pressure of component "i").

This law is only valid for **dilute** solutions.

If we double the total pressure P , the partial pressure p_i is also doubled. The result is the doubling of the concentration of component i in the liquid.



Constant temperature;
partial pressure: 1.0 and 2.0 bar



E.g. p_{O_2} in the air at 1.0 atm = $21/100 \times 1.0 = 0.21$ atm;

$$c_i = K_H(i) \times P_i$$

K_H units: M/atm ; ($K_H(O_2)$ value depends on the temperature)

$$c_{O_2} = K_H(O_2) \times 0.21 [M]$$

Fundamental types of Henry's law constants

There are many variants of Henry's law constants which can all be classified into two fundamental types:

- **one** possibility is to put the aqueous phase into the numerator and the gas phase into the denominator, i.e., define the constant as the quotient A/G .
- **Alternatively**, Henry's law constant can be defined as the quotient G/A , which results in the inverse value.

There is no advantage or disadvantage in using one or the other; the two types exist purely for historical reasons. Unfortunately, the name Henry's law constant is used for both types.

Atmospheric chemists often define the Henry solubility as:

$$H = C_a/p$$

- C_a is the concentration of a species in the aqueous phase;
- p is the partial pressure of that species in the gas phase under equilibrium conditions.

The SI unit for H is $\text{mol m}^{-3} \text{Pa}^{-1}$.

Here, "H" is expressed in terms of the concentration (C_a) of a species in the aqueous phase, and the partial pressure (p) of that species in the gas phase under equilibrium conditions.

In this case the notation is: $H = H^{cp}$

Reference: Sander, R., 2015. [Compilation of Henry's law constants \(version 4.0\) for water as solvent. Atmos. Chem. Phys. 15, 4399–4981. doi:10.5194/acp-15-4399-2015](https://doi.org/10.5194/acp-15-4399-2015)



The compilation contains 17 350 values of Henry's law constants for 4632 species, collected from 689 references.

Henry's law

$$H = Ca/p$$

Henry's K_H (solubilities) of trace gases have high potential importance in environmental chemistry (atmospheric chemistry, waste gas and waste water treatment, . . .) .

Q. Why CH_4 and CO_2 - the two most important (*) green-house gases - are not removed by the rain?

(*) **After water vapour!** Water vapour is a very effective absorber of IR radiations in the air, but it does not accumulate in the atmosphere. It has a very short atmospheric lifetime, hours to days, because it is rapidly removed mainly as rain. **The amount of water vapour that the atmosphere can hold increases as the atmosphere gets warmer, so the greenhouse properties of water vapour are usually considered to act as part of a feedback loop (i.e. a vicious circle), rather than a direct cause of climate change.**

WET DEPOSITION (washing of air pollutants) is more efficient for gas with high K_H !

E.g. ACID RAIN is the result of dissolution of gaseous inorganic air pollutants that behave as strong acids (mainly HNO_3 and H_2SO_4 ; secondary pollutants primarily formed by oxidation of NO_x and SO_2)

(1) M = molarity, i.e. mol/liter

(2) This constant accounts for HCHO (Formaldehyde) hydration, that is diol formation $H_2C(OH)_2$.

Henry's law constants (K_H) for some gases in water at 298 K.	
Species	K_H ($M atm^{-1}$) ($mole L^{-1} atm^{-1}$) ⁽¹⁾
O_2	1.7×10^{-3}
CH_4	1.0×10^{-3}
NO	1.9×10^{-3}
NO₂	7.0×10^{-3}
O_3	1.2×10^{-2}
CO_2	3.1×10^{-2}
Cl_2	0.9×10^{-1}
H_2S	1.1×10^{-1}
SO₂	1.2
CH_3CHO	6.7
NH_3	60
CH_3OH	2.2×10^2
HCl	2.5×10^3
HCHO ⁽²⁾	3.0×10^3
H_2O_2	9.9×10^4
HNO_3	2.1×10^5
H_2SO_4	∞
SO_3	∞

H
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Henry's law examples

EXAMPLE 01:

What is the partial pressure of O₂, p_{O₂}, if the total pressure, P, of air is 1.0 atmosphere and the O₂ content is 21% by volume?

Solution

$$x_i = V_i\% = 21/100 = 0.21$$

The partial pressure of O₂ is then: $p_i = x_i \cdot P = 0.21 \times 1.0 = 0.21 \text{ atm}$

EXAMPLE 02:

What is the concentration of CO₂ in a drop of rain in equilibrium with the atmosphere ($T=25^\circ\text{C}$; $P=1.0 \text{ atm}$; $\text{CO}_2 = 400 \text{ ppm (v,v)}$; $K_H = 0.0338 \text{ mol L}^{-1} \text{ atm}^{-1}$; $MW=44$)?

Partial pressure: $P_{\text{CO}_2} = x_{\text{CO}_2} \cdot P = 400 \cdot 10^{-6} \cdot 1.0 = 4.0 \cdot 10^{-4} \text{ atm}$

Henry: $K_H = c_{\text{CO}_2}/P_{\text{CO}_2}$

$$c_{\text{CO}_2} = K_H P_{\text{CO}_2} = (0.0338 \text{ mol L}^{-1} \text{ atm}^{-1}) (4.0 \cdot 10^{-4} \text{ atm})$$

$$c_{\text{CO}_2} = 13.5 \times 10^{-6} \text{ mol L}^{-1} = 13.5 \text{ } \mu\text{M}$$

$$c_{\text{CO}_2} = 44 \cdot 13.5 = 0.6 \text{ mg/L (= } 0.6 \text{ g/m}^3\text{)}$$

Henry's law examples

EXAMPLE 03:

An industrial gas flow contains HCHO (methanal; Formaldehyde). The ELV is 20 mg/Nm³. Convert it to ppm and calculate its partial pressure $K_{H(H_2CO,hydr.)} = 6.3 \times 10^3 \text{ M/atm}$. $MW = 30$. Calculate the aqueous methanal concentration in equilibrium.

Solution

A) Gas concentration

$$n_{HCHO} = 20 \text{ mg/Nm}^3 / 30 \text{ g/mol} = 0.66 \text{ mmol/Nm}^3 ;$$

$$V \text{ of } 1 \text{ mmol of gas} = 22.414 \text{ Ncm}^3 ;$$

$$[HCHO] = 0.66 \times 22.414 = 15 \text{ ppm}$$

B) Partial pressure

$$P_i = x_i \cdot P_{tot} = 15 \cdot 10^{-6} \text{ ppm} \times 1.0 \text{ atm} = 1.5 \cdot 10^{-5} \text{ atm}$$

C) Liquid concentration

$$C_i = K_H \times P_i = 6.3 \times 10^3 \times 1.5 \cdot 10^{-5} = 0.0945 \text{ M}$$

One minute of relax



One minute of relax... While much of the focus in the automotive industry is on reducing exhaust emissions, there is another cause of emissions. The fuel in a vehicle's tank and fuel lines is subject to evaporation over time, releasing volatile organic compounds into the atmosphere (***this applies to gasoline, not to diesel!***). Evaporative emission control (EVAP) systems have become commonplace in all new vehicles: Euro 5/6 regulations continue the Euro 4 limits (Directive 98/69/EC) of **2 grams of evaporative emissions per day** (U.S. regulations limit evaporative emissions to 0.5 grams per day).

To reduce gasoline evaporative emission in the sunny hours, you could park freely in a garage, under a tree, ... **NOT** under the sun.

Note: There is evidence that in many cases the evaporative emissions control systems are designed just to pass the legislative test.

VOC composition of current motor vehicle fuels

Fuel Unit	Gasoline (mg L ⁻¹)	E85 (mg L ⁻¹)	E85/Gasoline (%)	Diesel (mg L ⁻¹)	B20 (mg L ⁻¹)	B20/Diesel (%)
<i>Aromatics</i>						
Benzene	6140	862	14	67	37	55
Toluene	15,400	4110	27	238	214	90
Ethylbenzene	3080	1990	65	124	186	150
p-Xylene,m-xylene	9120	6980	76	420	496	118
o-Xylene	4610	2790	60	185	212	115
Isopropylbenzene	351	156	45	44	70	160
n-Propylbenzene	2110	665	32	115	167	146
p-Isopropyltoluene	88	29	33	112	83	75
4-Ethyl toluene	8380	2650	32	400	464	116
2-Ethyl toluene	3460	928	27	194	264	136
1,3,5-Trimethylbenzene	4060	1030	25	202	150	74
1,2,4-Trimethylbenzene	10,600	3270	31	720	575	80
1,2,3-Trimethylbenzene	3950	975	25	2120	961	45
sec-Butylbenzene	159	65	41	90	117	130
n-Butylbenzene	822	198	24	375	111	30
Styrene	14	4	32	<0.02	<0.02	–
Naphthalene	2240	378	17	3000	1220	41
<i>Alkanes</i>						
n-Heptane	12,800	3330	26	174	138	79
n-Octane	2870	1550	54	481	612	127
n-Nonane	1790	1050	59	7020	4120	59
n-Decane	1390	262	19	7690	4310	56
n-Undecane	1120	121	11	7730	4560	59
n-Dodecane	822	85	10	8370	5000	60
n-Tridecane	644	80	12	13,400	7620	57
n-Tetradecane	213	19	9	10,100	7130	71
n-Pentadecane	62	<0.02	–	9030	7580	84
n-Hexadecane	18	<0.02	–	9300	5550	60
Cyclohexane	9830	880	9	191	69	36
Methyl cyclohexane	8280	778	9	426	270	63
Total target VOCs	114,000	34,900	31	80,700	51,600	64

<: Below method detection limit, limit of detection is listed in supplemental data Table A.1.

Chin, J.-Y., Batterman, S.A., 2012. VOC composition of current motor vehicle fuels and vapors, and collinearity analyses for receptor modeling. *Chemosphere* 86, 951–958. <https://doi.org/10.1016/j.chemosphere.2011.11.017>.VOC

Gas/liquid equilibrium: saturation (it refers to any gas-vapour system)

Absolute saturation S

$$H = \frac{m_i}{m_{dry\ air}} = \frac{MW_i * n_i}{29 * (n - n_i)} = \frac{MW_i * p_i}{29 * (p - p_i)}$$

- n_i = moles of species i; MW_i = molecular weight of species i
- n = total number of moles in gas
- p_i = partial pressure of species i
- p = total gas pressure

Relative saturation SH

Relative saturation SH (%): measure of partial pressure of species i with respect to maximum allowable content (saturation conditions) at the same T

$$RH(\%) = 100 * \frac{p_i}{p_{v,i}^{\circ}}$$

- $p_{v,i}^{\circ}$ = vapor pressure of species i

Gas/liquid equilibrium: humidity (it refers to air-water system)

Absolute humidity H

$$H = \frac{m_{H_2O}}{m_{dry\ air}} = \frac{18 * n_{H_2O}}{29 * (n - n_{H_2O})} = \frac{18 * p_{H_2O}}{29 * (p - p_{H_2O})}$$

- n_{H_2O} = moles of water vapor
- n = total number of moles in gas
- p_{H_2O} = partial pressure of water vapor
- p = total gas pressure

Relative humidity RH

Relative humidity RH (%): measure of water vapor content with respect to maximum allowable content (saturation conditions) at the same T

- ratio between partial pressure of water vapor in the gas and vapor pressure of water vapor at T gas
- at **constant H**, RH **increases** with **decreasing T**: when **RH = 100%**, **saturation** is reached and **T = dew point**

$$RH(\%) = 100 * \frac{p_{H_2O}}{p_{v,H_2O}^o}$$

0% means the air is completely dry, and **100%** means the air contains all the water it can hold in the present circumstances and it cannot absorb any more water (from any source).

Exercise 1.8. Humidity

Assuming a temperature of $t=110\text{ }^{\circ}\text{C}$, a total pressure of 1 atm and a absolute humidity of 0.1 kg water/kg dry air, estimate the relative humidity?

For the vapor pressure of water use the following table:

Temperature [$^{\circ}\text{C}$]	Water saturation pressure		
	[kPa], [100*bar]	[atm]	[psi]
0.01	0.61165	0.0060	0.088712
2	0.70599	0.0070	0.10240
4	0.81355	0.0080	0.11800
10	1.2282	0.0121	0.17814
14	1.5990	0.0158	0.23192
18	2.0647	0.0204	0.29946
20	2.3393	0.0231	0.33929
25	3.1699	0.0313	0.45976
30	4.2470	0.0419	0.61598
34	5.3251	0.0526	0.77234
40	7.3849	0.0729	1.0711
44	9.1124	0.0899	1.3216
50	12.352	0.122	1.7915
54	15.022	0.148	2.1788
60	19.946	0.197	2.8929
70	31.201	0.308	4.5253
80	47.414	0.468	6.8768
90	70.182	0.693	10.179
96	87.771	0.866	12.730
100	101.42	1.001	14.710
110	143.38	1.42	20.796
120	198.67	1.96	28.815
130	270.28	2.67	39.201
140	361.54	3.57	52.437
150	476.16	4.70	69.061
160	618.23	6.10	89.667
180	1002.8	9.90	145.44
200	1544.9	15.35	225.52

At the same conditions but with a temperature of 50°C how does the relative humidity change?

source: https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html)

Gas/liquid equilibrium: vapor condensation (dew point)



$$p_i < p_{v,i}^{\circ} \quad \text{---} \quad \text{---} \quad \blacktriangleright$$

$$p_i > p_{v,i}^{\circ}$$



- p_i = partial pressure of "i" = $y_i \cdot p$
- $p_{v,i}^{\circ}$ = vapor pressure of "i" (vapor pressure of pure component "i") .
 - gas phase **partial pressure of "i"** in equilibrium with **pure liquid solution**
 - dependent on "i" and on **T**

Antoine's law:

$$\ln p_{v,i}^{\circ} = A - \frac{B}{T + C}$$

A, B, C = numerical constants
T = temperature

- vapor condensation when:
 - **T** is **reduced** at constant pressure and composition (gas cooling)
 - **p** is increased at constant temperature and composition (gas compression)
- **dew point**: temperature **T** where $p_i = p_{v,i}^{\circ} \rightarrow$ formation of **vapor droplets**

In other words , the partial pressure (p_i) at the given temperature is equal to the vapor pressure ($p_{v,i}^{\circ}$) at the dew-point temperature.

So if $p_i < p_{v,i}^{\circ}$ the water content (or acid gas) in the flue gas is below the saturation level.

Antoine's law

Antoine equation constants, $\log_{10} p = A - \frac{B}{T + C}$, p in mm Hg, T in °C

Substance	Formula	Range, °C	A	B	C
Acetaldehyde	C ₂ H ₄ O	-45 to +70	6.81089	992.0	230
Acetic acid	C ₂ H ₄ O ₂	0 to +36	7.80307	1651.1	225
		+36 to +170	7.18807	1416.7	211
Acetone	C ₃ H ₆ O	—	7.02447	1161.0	224
Ammonia	NH ₃	-83 to +60	7.55466	1002.711	247.885
Benzene	C ₆ H ₆	—	6.90565	1211.033	220.790
Carbon tetrachloride	CCl ₄	—	6.93390	1242.43	230.0
Chlorobenzene	C ₆ H ₅ Cl	0 to +42	7.10690	1500.0	224.0
		+42 to +230	6.94504	1413.12	216.0
Chloroform	CHCl ₃	-30 to +150	6.90328	1163.03	227.4
Cyclohexane	C ₆ H ₁₂	-50 to +200	6.84498	1203.526	222.863
Ethyl acetate	C ₄ H ₈ O ₂	-20 to +150	7.09808	1238.71	217.0
Ethyl alcohol	C ₂ H ₆ O	—	8.04494	1554.3	222.65
Ethylbenzene	C ₈ H ₁₀	—	6.95719	1424.255	213.206
<i>n</i> -Heptane	C ₇ H ₁₆	—	6.90240	1268.115	216.900
<i>n</i> -Hexane	C ₆ H ₁₄	—	6.87776	1171.530	224.366
Lead	Pb	525 to 1325	7.827	9845.4	273.15
Mercury	Hg	—	7.975756	3255.61	281.988
Methyl alcohol	CH ₄ O	-20 to +140	7.87863	1473.11	230.0
Methyl ethyl ketone	C ₄ H ₈ O	—	6.97421	1209.6	216
<i>n</i> -Pentane	C ₅ H ₁₂	—	6.85221	1064.63	232.000
Isopentane	C ₅ H ₁₂	—	6.78967	1020.012	233.097
Styrene	C ₈ H ₈	—	6.92409	1420.0	206
Toluene	C ₇ H ₈	—	6.95334	1343.943	219.377
Water	H ₂ O	0 to 60	8.10765	1750.286	235.0
		60 to 150	7.96681	1668.21	228.0

Wet-bulb and dry-bulb temperature

Dry Bulb Temperature (T_{db}). The Dry Bulb temperature, usually referred to as "air temperature", is the air property that is most commonly used. When people refer to the temperature of the air they are normally referring to the dry bulb temperature. In meteorology and psychrometrics the word temperature by itself without a prefix usually means dry-bulb temperature.

The Dry Bulb Temperature refers basically to the ambient air temperature. It is called "Dry Bulb" because the air temperature is indicated by a thermometer not affected by the moisture of the air. Dry-bulb temperature - T_{db} , can be measured using a normal thermometer freely exposed to the air but shielded from radiation and moisture.

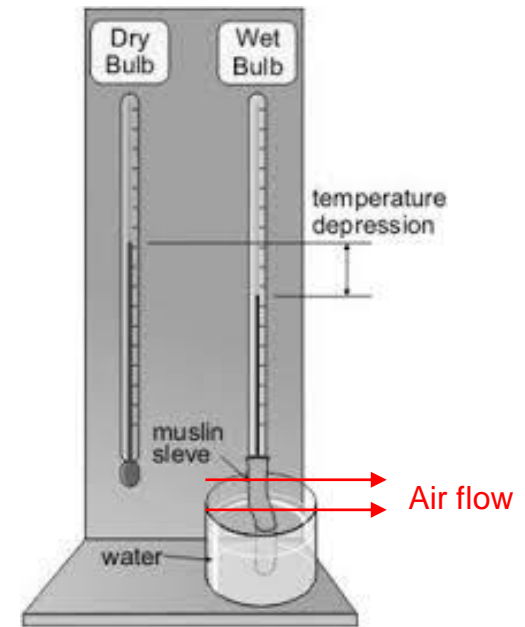
Wet Bulb Temperature (T_{wb}). The thermodynamic wet-bulb temperature is a thermodynamic property of a mixture of air and water vapor. The Wet Bulb temperature is the adiabatic saturation temperature.

Wet Bulb temperature can be measured by using a thermometer with the bulb wrapped in wet muslin. As water in the cloth evaporates, it lowers the temperature. This is the idea behind evaporative coolers. This is important because the more moisture the air contains, the less evaporation occurs. The amount of moisture the air can contain is a function of the temperature of the air. Cold air can't contain as much moisture as warm air.

The key here is that if the air is totally saturated with moisture, which doesn't happen often except in fog, the humidity is 100%. When the humidity is 100%, it can't absorb more moisture without first losing moisture, so no water evaporates and the wet bulb temperature is the same as the dry bulb temperature.

The Wet Bulb temperature is always between the Dry Bulb temperature and the Dew Point. For the wet bulb, there is a dynamic equilibrium between heat gained because the wet bulb is cooler than the surrounding air and heat lost because of evaporation.

The wet bulb temperature is the temperature of an object that can be achieved through evaporative cooling, assuming good air flow and that the ambient air temperature remains the same.



The difference of temperature depends on the water evaporation from the wet muslim and therefore to the capacity of the air to hold vapour water (i.e. Relative humidity). If the air is saturated ($HR=100\%$), it can't contain further water and no evaporation can occur.

Dew point temperature

Dew temperature: That temperature at which water vapour present in the atmosphere is just sufficient to saturate it. When air is cooled below the dew point, the excess of water vapour appears as tiny droplets or crystals of ice depending on the temperature of the air mass. Above this temperature the moisture stays in the air.

This term is also applicable to acid gases as in the problem of acid corrosion and acid smut formation.

The **acid dewpoint** (also acid dew point) of a flue gas (i.e., a combustion product gas) is the temperature, at a given pressure, at which any gaseous acid in the flue gas will start to condense into liquid acid.

The acid dew point of a flue gas, at a given pressure, is often referred to as the point at which the flue gas is "saturated" with gaseous acid, meaning that the flue gas cannot hold any more gaseous acid.

In many industrial combustion processes, the flue gas is cooled by the recovery of heat from the hot flue gases before they are emitted to the atmosphere from the final flue gas stack. **It is very important not to cool the flue gas below its acid dew point** because the resulting liquid acid condensed from the flue gas can cause serious corrosion problems for the equipment used in transporting, cooling and emitting the flue gas.



If temperatures are above the dew point, there is no dew formation.

If the temperature is below the dew point, there is dew.

While it may seem that wet bulb temperature and dew point temperature are the same things, they are not. An easy way to put this would simply be that wet bulb temperature is a measurement of evaporation in relation to temperature. Dew point temperature is a measurement of condensation in relation to temperature. Evaporation and condensation are nearly opposites, so wet bulb and dew point are quite different.

Both wet bulb temperature and dew point temperature are important to understanding the current air conditions, though the two measurements are not the same.

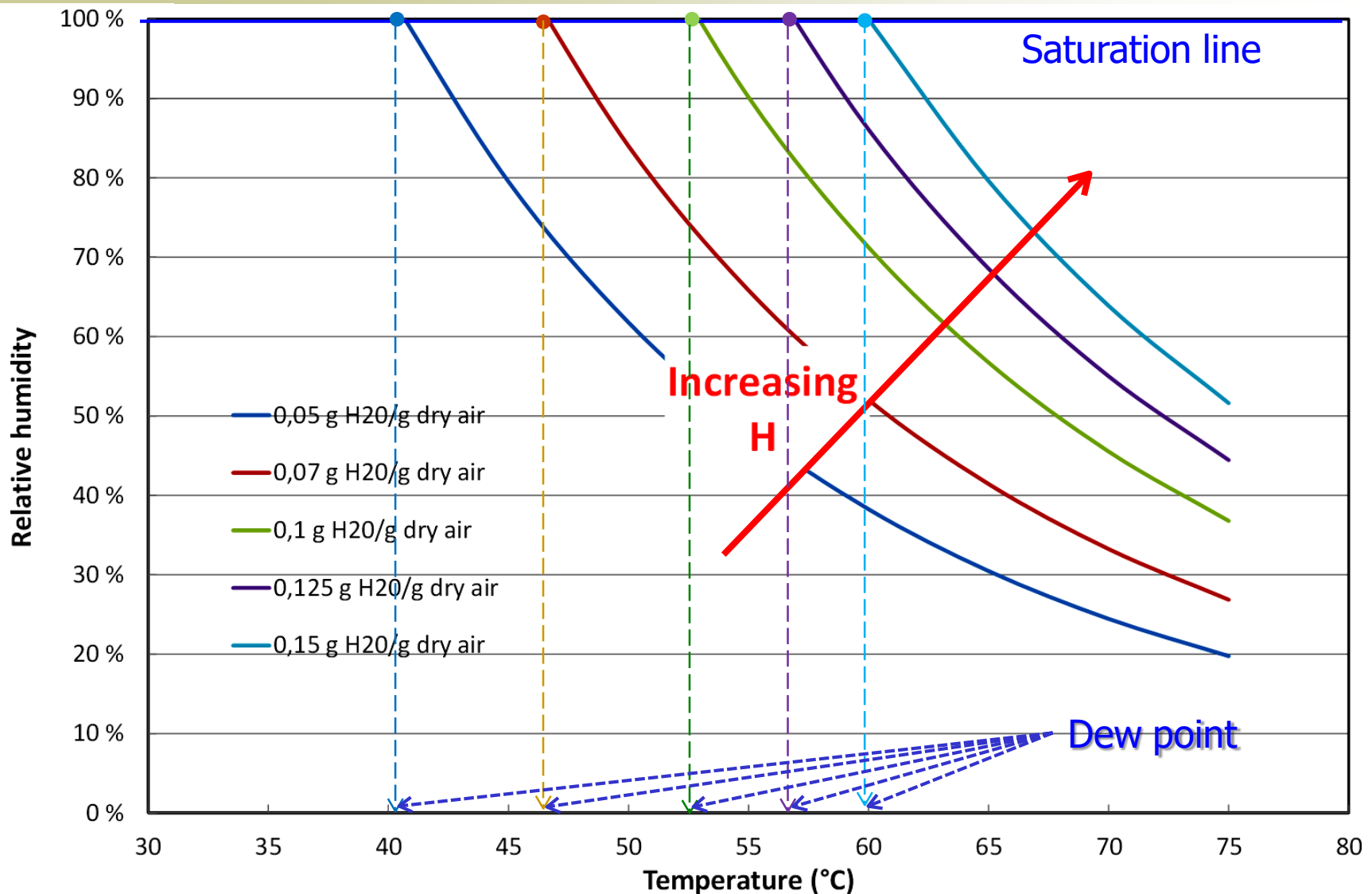
When the air is saturated, the dewpoint is equal to the wet bulb temperature and the actual temperature. In unsaturated air, the dewpoint is always a lower temperature than the wet bulb temperature.

Info...

The following slides on ARE NOT INCLUDED IN THE APC PROGRAMM, BUT VERY USEFUL FOR YOU.

They help You to understand the meaning of “GAS FLOW QUENCHING”: **old Waste System used to install a Quencher upstream**, to regulate the inlet temperature, or in case of malfunctioning, ...and avoid Waste System collapse in case of too hot inlet WG! ...not so infrequent accident when treating flue gases!

Gas/liquid equilibrium: humidity (water vapor content)



at constant H, RH increases with decreasing T: when RH = 100%, saturation is reached and T = dew point

Dew point temperature: calculations for acid gases

Sulfuric acid (H_2SO_4) dew point: [\[1\]](#) [\[2\]](#)

$$(1) 1000/T = 1.7842 - 0.0269 \cdot \log_{10}(P_{H_2O}) - 0.1029 \cdot \log_{10}(P_{SO_3}) + 0.0329 \cdot \log_{10}(P_{H_2O}) \cdot \log_{10}(P_{SO_3})$$

or this equivalent form: [\[3\]](#) [\[4\]](#)

$$(2) 1000/T = 2.276 - 0.02943 \cdot \ln(P_{H_2O}) - 0.0858 \cdot \ln(P_{SO_3}) + 0.0062 \cdot \ln(P_{H_2O}) \cdot \ln(P_{SO_3})$$

Sulfurous acid (H_2SO_3) dew point: [\[5\]](#) [\[6\]](#)

$$(3) 1000/T = 3.9526 - 0.1863 \cdot \ln(P_{H_2O}) + 0.000867 \cdot \ln(P_{SO_2}) + 0.000913 \cdot \ln(P_{H_2O}) \cdot \ln(P_{SO_2})$$

Hydrochloric acid (HCl) dew point: [\[7\]](#) [\[8\]](#)

$$(4) 1000/T = 3.7368 - 0.1591 \cdot \ln(P_{H_2O}) - 0.0326 \cdot \ln(P_{HCl}) + 0.00269 \cdot \ln(P_{H_2O}) \cdot \ln(P_{HCl})$$

Nitric acid (HNO_3) dew point: [\[9\]](#)

$$(5) 1000/T = 3.6614 - 0.1446 \cdot \ln(P_{H_2O}) - 0.0827 \cdot \ln(P_{HNO_3}) + 0.00756 \cdot \ln(P_{H_2O}) \cdot \ln(P_{HNO_3})$$

where:

T = The acid dew point temperature for the indicated acid, in kelvins

P = Partial pressure, in atmospheres for equation 1 and in mmHg for equations 2, 3, 4 and 5

REFERENCES:

1. F.H. Verhoff and J.T. Banchero (1974), "Predicting Dew Points of Gases", Chemical Engineering Progress, Vol. 78, Issue 8, pp. 71 - 72
2. R.R. Pierce (1977), "Estimating Acid Dewpoints in Stack Gases", Chemical Engineering, Vol. 84, Issue 8, pp. 125 - 128
3. Same as References 2 and 4.
4. V. Ganapathy (1993), Steam Plant Calculations Manual, 2nd Edition, CRC Press, ISBN 0-8247-9147-9. See Table 2.9 on page 94. Available online here in Google Books.
5. Same as References 2 and 8.
6. Yen Hsiung Kiang (1981), "Predicting Dewpoints of Gases", Chemical Engineering Vol. 88, Issue 3, p. 127
7. Same as References 2 and 8.
8. Yen Hsiung Kiang (1981), "Predicting Dewpoints of Gases", Chemical Engineering Vol. 88, Issue 3, p. 127
9. Same as References 8 and 12.

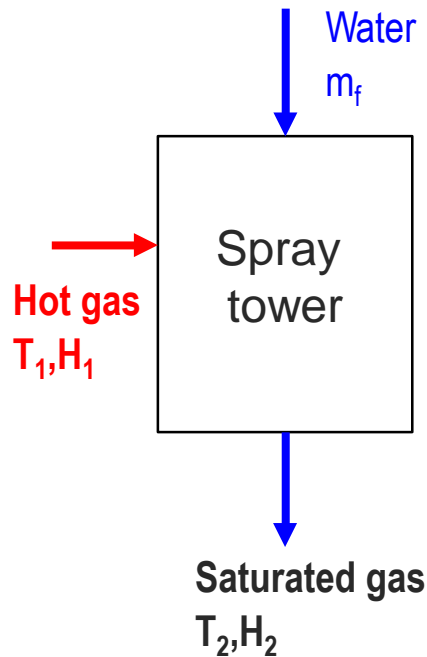
<https://chemengineering.wikispaces.com/Acid+dewpoint>

Exercise 1.9. Acid Dew Point

Because of the presence of gaseous sulfuric acid, the sulfuric acid dew point of most flue gases is much higher than the water dew point of the flue gases.

- Calculate the water dew point for a flue gas with 12 volume % water vapour and containing no acid gases.
- Calculate the dew point of the same flue gas with the addition of only 4 ppmv (0.0004 volume %) of SO_3 .

Cooling by water mixing



Cooling of hot gases: T reduction, volume flow rate reduction

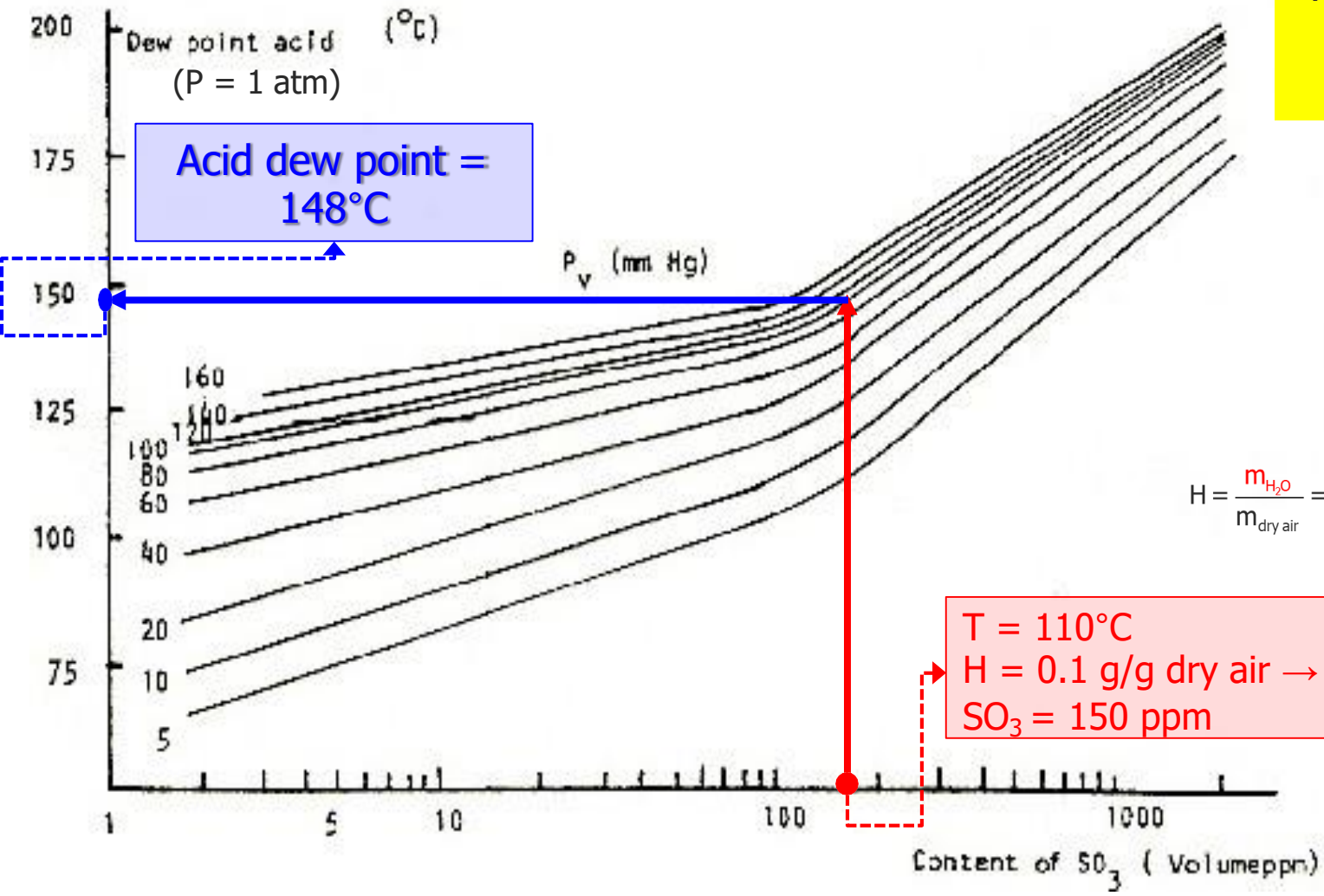
Liquid water mixing (spraying): **increase** in absolute humidity H (gas heat removed by heat of **vaporization** of water) → **saturation**

- moisture formation **with clogging and plugging risks**
- **visible plumes** at stack discharge, **water droplets deposition**
- acids formation **with corrosion risks** → significant **increase of dew points** with **small amounts** of acid gases (especially SO_3)

- Assume an adiabatic process. All the heat energy is used for the evaporation of the water
- Which will be the new temperature of T_2 of the saturated gas?
- Is this temperature higher or lower than the dew point?

Cooling by water mixing: acid dew point

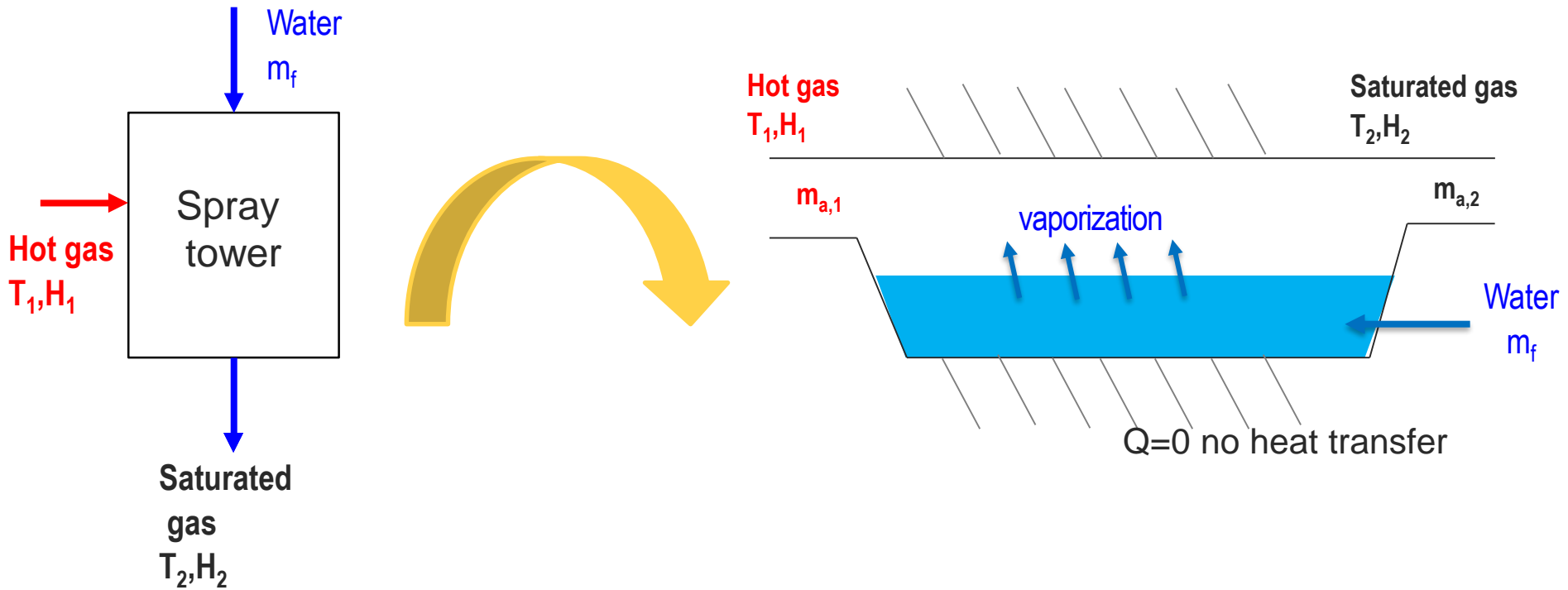
The dew point without any acid gas is around 53°C



$$H = \frac{m_{H_2O}}{m_{dry\ air}} = \frac{18 \cdot n_{H_2O}}{29 \cdot (n - n_{H_2O})} = \frac{18 \cdot p_{H_2O}}{29 \cdot (p - p_{H_2O})}$$

T = 110°C
H = 0.1 g/g dry air → $p_v = 105$ mm Hg
SO₃ = 150 ppm

Cooling by water mixing (adiabatic saturation of air – both clean air and polluted air)



Mass balance applied to water

$$m_{v,1} + m_f = m_{v,2}$$

Considering that $H = m_v / m_{a,dry}$ and

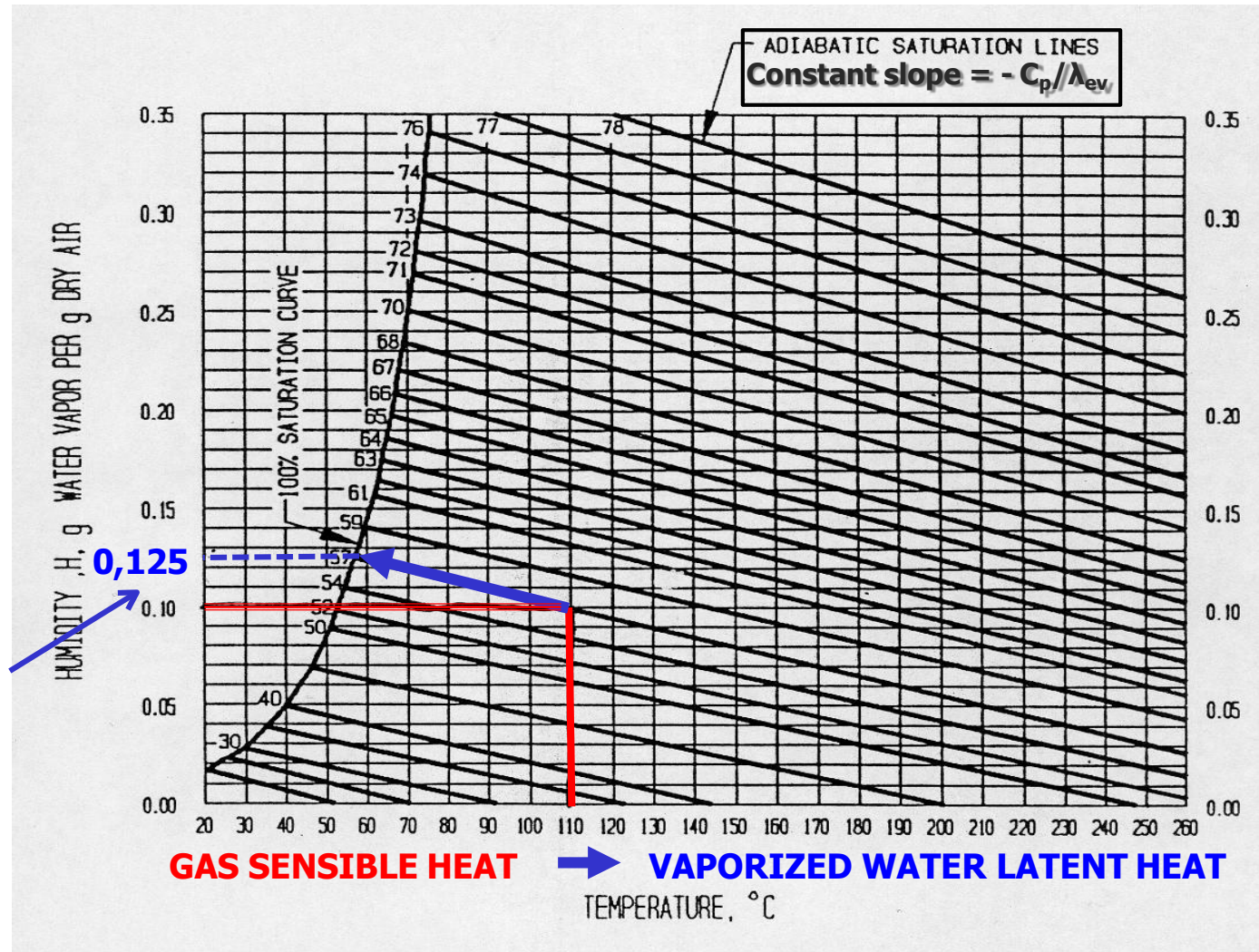
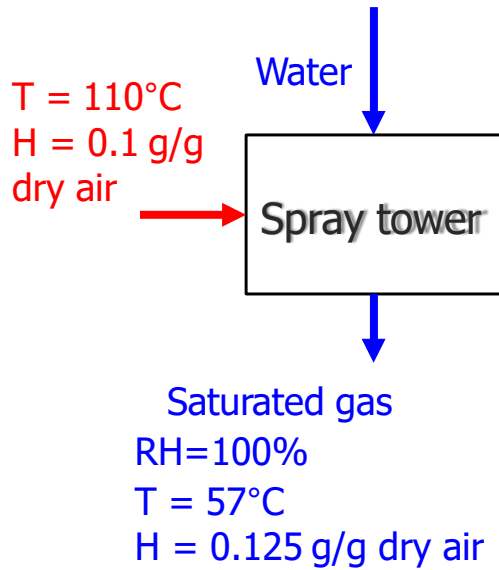
$$m_{a,dry,1} = m_{a,dry,2} = m_{a,dry}$$

$$m_{a,dry,1} * H_1 + m_f = m_{a,dry,2} * H_2 \quad m_f = m_{a,dry} * (H_1 - H_2)$$

+ Energy conservation

The air saturation, occurs under adiabatic conditions

1° approach: psychrometric chart



2° approach: energy balance

Specific enthalpy, h , is the enthalpy of moist air referred to 1 kg of dry air (kJ/kg).

The formula used is: $h = h_{\text{dry air}} + \text{heat}_{\text{water vapor}} = 1.005 \cdot t + x \cdot (1.82 \cdot t + 2501)$

$h =$ **Enthalpy of the moist air**, that is the mixture (air+water vapour) (kJ/kg dry air)

$t =$ Temperature ($^{\circ}\text{C}$)

$x =$ Weight (mass) fraction of water (i.e. **kg of water vapor/kg dry air**) ($0 \leq x \leq 1$)

DRY AIR

In the temperature range $10 \div 50^{\circ}\text{C}$, with negligible error, **dry air** can be treated as an ideal gas with a constant c_p (specific heat of air at constant pressure) value of 1.005 kJ/kg $^{\circ}\text{C}$. Taking 0°C as the reference temperature, the enthalpy of dry air can be determined from

$$h_{\text{dry air}} = c_p t = 1.005 \cdot t \quad [\text{kJ}/(\text{kg}_{\text{dry air}} \cdot ^{\circ}\text{C}) \times ^{\circ}\text{C} = \text{kJ}/\text{kg}_{\text{dry air}}]$$

WATER VAPOR

The enthalpy of water vaporization (latent heat) at 0°C is 2501 kJ/kg.

The average c_p **value of water vapor** in the temperature range $10 \div 50^{\circ}\text{C}$ can be taken to be 1.82 kJ/kg $^{\circ}\text{C}$. (different values, such as 1.84 or 1.88, can be found in the literature).]

$$\text{heat}_{\text{water vapor}} = 1.82 \cdot t + 2501 \quad [\text{kJ}/\text{kg}_{\text{water vapor}}]$$

$x \equiv H$, HUMIDITY RATIO

2° approach: energy balance

*The air saturation, occurs under adiabatic conditions, that is $\Delta H \equiv 0$, or $h_1 = h_2$; the cooling of unsaturated initial air (at a temperature, t_1 , called **dry bulb temperature**) provides the heat necessary for the vaporization of the additional liquid water to saturate the air and heating the produced vapour up to the saturation temperature t_2 , (called **wet bulb temperature**):*

$$1.005 * t_1 + x_1(1.84 t_1 + 2501) = 1.005 * t_2 + x_2(1.84 t_2 + 2501)$$

Where t_1 and x_1 are known or can be easily calculated.

You can't, of course, "solve" the above single equation with two variables (t_2, x_2)!

We should, however, remember that t_2 corresponds to air saturation (wet bulb) temperature at constant enthalpy ($h_1 = h_2$).

WE PROCEED IN THIS WAY:

1ST: CALCULATE h_1 (enthalpy of moist^(*) air before humidification with additional water);

() before humidification, the air can be dry, but this will not occur in the real applications!. Outside air, and industrial flue gases always contain some water.*

2ND: DETERMINE THE WET BULB TEMPERATURE, $T_{\text{wet bulb}}$. Since $h_2 = h_1$, we can find the T_{wb} , either graphically (the point of interception of line of constant enthalpy h_1 with the air saturation curve in a "Psychrometric chart" (many in internet!), or

through a "Psychrometric calculator" (many in internet!), INPUT DATA: h_1 value; OUTPUT DATA: **Wet-Bulb Temperature.**

3RD: DETERMINE THE WATER BALANCE. The amount of water for saturation is often required, in the design of waste gas treatments.

The specific amount of fed water, x_f , that is the amount of water to be added for 1 kg of dry air is easily obtained by the expression: $x_f = x_2 - x_1$

2° approach: energy balance

$$h_1 = 1.005 \cdot t_1 + x_1(1.84 t_1 + 2501)$$

$$t_1 = 110^\circ \text{ C}$$

$$x_1 = m_{\text{H}_2\text{O}} / m_{\text{dry air}} = 18 \cdot p_{\text{H}_2\text{O}} / 29 \cdot (p - p_{\text{H}_2\text{O}}) = 0,1 \text{ g water/g dry air}$$

Where:

- $p_{\text{H}_2\text{O}}$ = partial pressure of water vapor
- p = total gas pressure = 1 atm = 98070 Pa

RH is can be estimated by the information of H (see exercise 1,8) - RH = 9.5

Therefore:

$$h_1 = 380,89 \text{ kJ/kg}; h_2 = 380,89 \text{ kJ/kg};$$

$$t_{\text{wb}} = 56^\circ \text{ C (from psychrometric calculator);}$$

$$x_2 = 0.124 \text{ kg}_{\text{water vapor}} / \text{kg}_{\text{dry air}}$$

$$\text{H}_2\text{O for saturation: } 0.124 - 0.1 = 24 \text{ g w /kg dry air}$$

$$\Delta T_{\text{air flow}} = 110 - 56 = 54^\circ \text{ C}$$

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Psychrometric Calculations

The formulations used here to calculate moist air properties are based on perfect gas relations published in 1989 [ASHRAE](#) Fundamentals Handbook, which should be accurate. Nevertheless, It is strongly recommend that you to compare the results calculated by this worksheet with a psychrometric chart. There is **no error checking** so you should use reasonable input values.

Inputs

Outputs

Unit Chosen:	<input checked="" type="radio"/> SI	<input type="radio"/> IP			
Parameter Name	Value	Unit	Atmospheric Press	1.01323875979	bar
Dry Bulb Temp.:	110	C	Sat. Vapor Press.	1433.83206329	mbar
Wet Bulb Temp.:	<input type="radio"/> 55.9862524867	C	Partial Vapor Press.	136.214046013	mbar
Relat. Humidity:	<input checked="" type="radio"/> 9.5	%	Humidity Ratio	0.09660518716	kg/kg
Dew Point Temp	<input type="radio"/> 51.9779587389	C	Enthalpy	371.671925745	kJ/kg
Altitude	0.0	m	Specific Volume	1.24849853645	m ³ /kg
<input type="button" value="Calculate"/>			<input type="button" value="©"/>		

Expert Engineering Advice

You may want some expert engineering advice on [Spray Ponds](#) or on [Cooling Towers](#), if so please feel free to [contact](#) us.

<http://www.sugartech.co.za/psychro/index.php>

EXAMPLES: Wet scrubber

Unsaturated air entering a wet scrubber has: t_1 (dbt_{emp}) = 20°C ; RH, relative humidity = 50% (v/v). Calculate: h_1 , h_2 (sat.), t_{wetbulb} , x_1 , and x_2 .

ANSWERS:

$$h_1 = 1.005 \cdot t_1 + x_1(1.84 t_1 + 2501)$$

$$t_1 = 20^\circ \text{C}$$

$$x_1 = m_{\text{H}_2\text{O}} / m_{\text{dry air}} = 18 \cdot p_{\text{H}_2\text{O}} / 29 \cdot (p - p_{\text{H}_2\text{O}})$$

Where:

- $p_{\text{H}_2\text{O}}$ = partial pressure of water vapor
- p = total gas pressure = 1 atm = 98070 Pa

The partial pressure of water vapour can be estimated by the information of $\text{RH} = 100 \cdot (p_{\text{H}_2\text{O}} / p_{v,\text{H}_2\text{O}})$

The $p_{v,\text{H}_2\text{O}}$ at 20°C is tabulated and equal to 2265 Pa (see next slide), therefore $p_{\text{H}_2\text{O}}$ is equal to 1132 Pa.

$$x_1 = (18 \cdot 1132) / (29 \cdot (98070 - 1132))$$

$$x_1 = 0,0073 \text{ kg}_{\text{water vapor}} / \text{kg}_{\text{dry air}}$$

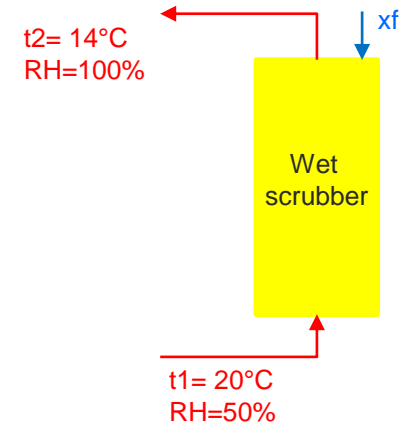
$$h_1 = 38.7 \text{ kJ/kg}; h_2 = 38.7 \text{ kJ/kg};$$

$$t_{\text{wb}} = 14^\circ \text{C} \text{ (from psychrometric calculator);}$$

$$x_2 = 0.0098 \text{ kg}_{\text{water vapor}} / \text{kg}_{\text{dry air}}$$

$$\text{H}_2\text{O abs for saturation: } 0.0098 - 0.0073 = 2.5 \text{ g w /kg dry air}$$

$$\Delta T_{\text{air flow}} = 14 - 20 = -6^\circ \text{C}$$



Water saturation pressure

Temperature [°C]	Water saturation pressure		
	[kPa], [100*bar]	[atm]	[psi]
0.01	0.61165	0.0060	0.088712
2	0.70599	0.0070	0.10240
4	0.81355	0.0080	0.11800
10	1.2282	0.0121	0.17814
14	1.5990	0.0158	0.23192
18	2.0647	0.0204	0.29946
20	2.3393	0.0231	0.33929
25	3.1699	0.0313	0.45976
30	4.2470	0.0419	0.61598
34	5.3251	0.0526	0.77234
40	7.3849	0.0729	1.0711
44	9.1124	0.0899	1.3216
50	12.352	0.122	1.7915
54	15.022	0.148	2.1788
60	19.946	0.197	2.8929
70	31.201	0.308	4.5253
80	47.414	0.468	6.8768
90	70.182	0.693	10.179
96	87.771	0.866	12.730
100	101.42	1.001	14.710
110	143.38	1.42	20.796
120	198.67	1.96	28.815
130	270.28	2.67	39.201
140	361.54	3.57	52.437
150	476.16	4.70	69.061
160	618.23	6.10	89.667
180	1002.8	9.90	145.44
200	1554.9	15.35	225.52

https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html

Psychrometric calculator

<http://www.sugartech.co.za/psychro/index.php>

ADIABATIC SATURATION OF AIR: HOME EXERCISES

Calculate:

Unsaturated air entering a wet scrubber has: t_1 (dbt_{emp}) = 90° C ; RH, relative humidity = 50% (v/v). Calculate: h_1 , h_2 (sat.), $t_{wetbulb}$, x_1 , and x_2 .

Unsaturated air entering a wet scrubber has: t_1 (dbt_{emp}) = 110° C ; H, absolute humidity = 1 g/g. Calculate: h_1 , h_2 (sat.), $t_{wetbulb}$, x_1 , and x_2 .

Wet Scrubber – AVOID HIGH INLET TEMPERATURES!

- In general, the higher the gas temperature, the lower the absorption rate from gas to liquid.
- Excessively high gas temperatures lead to significant solvent or scrubbing liquid loss through evaporation → (higher amounts of H_2O in the cleaned gas!)
- More expensive materials withstanding high temperatures are required for the WS.

ACIDITY

Acidity

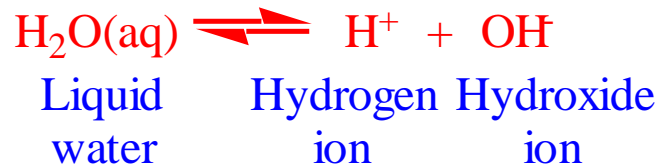
Measure of the concentration of hydrogen ions (H⁺) in solution

$$\text{pH} = -\log_{10}[\text{H}^+]$$

[H⁺] = molarity (M, moles of H⁺ per liter of solution)

Higher [H⁺] --> lower pH --> more acidic solution

In dilute water, the only source of H⁺ is



$$[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}^2 \text{ --> } [\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

$$\text{--> pH} = -\log_{10}[10^{-7}\text{M}] = 7$$

Acid and bases

Acid

Substance that, when added to a solution, dissociates, increasing $[H^+]$, decreasing pH

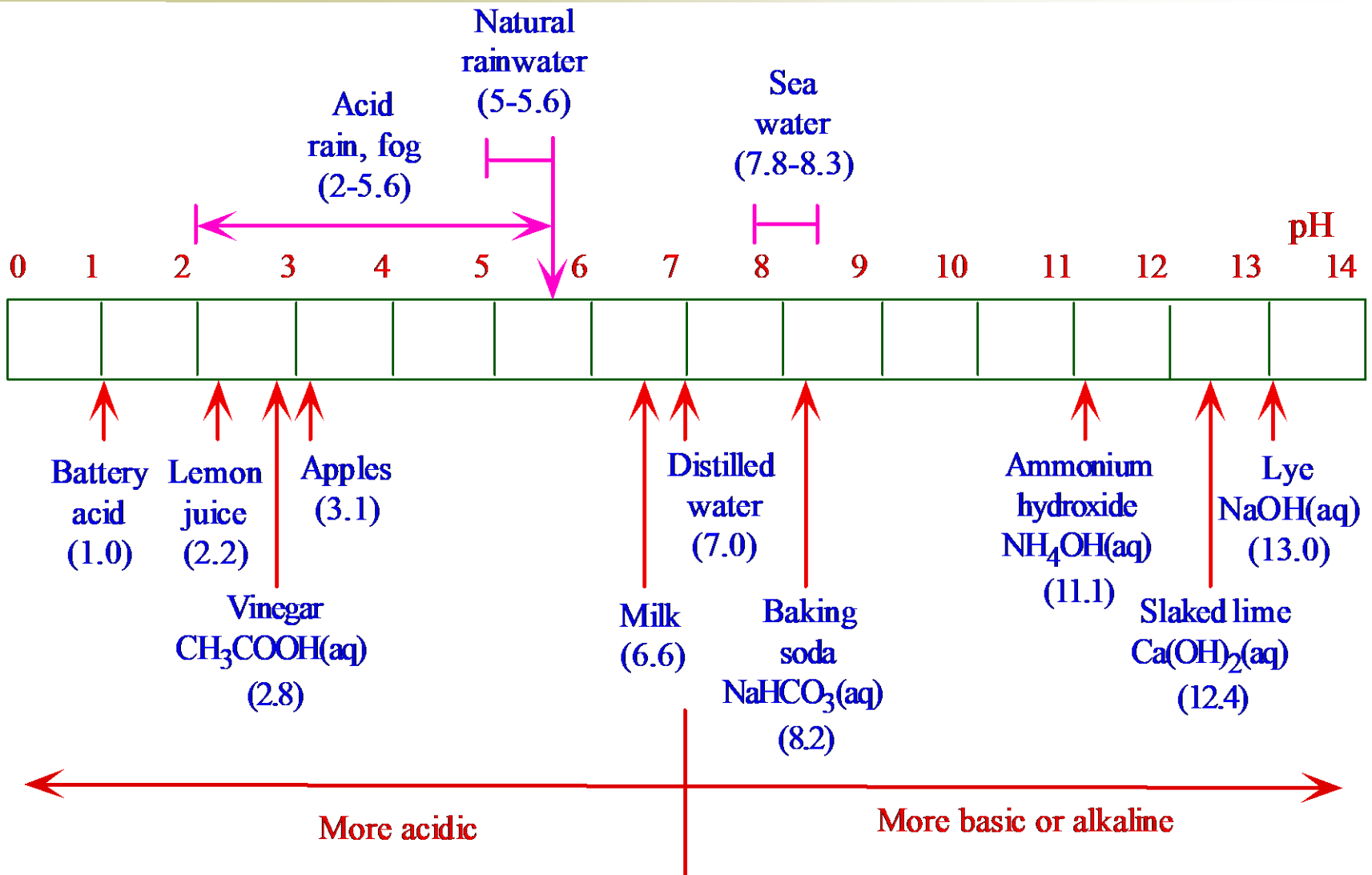
Strong acid: Substances that dissociate readily
(e.g., H_2SO_4 , HCl , HNO_3)

Weak acids: Substances that dissociate less readily
(e.g., H_2CO_3)

Base (alkalis)

Substances that, when added to a solution, reduce $[H^+]$, increasing pH. (e.g., $NH_3(aq)$, $Ca(OH)_2(aq)$)

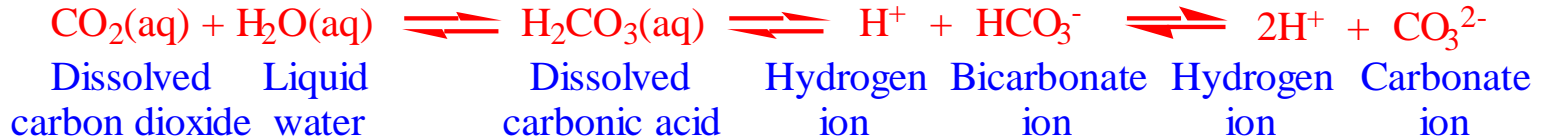
pH Scale



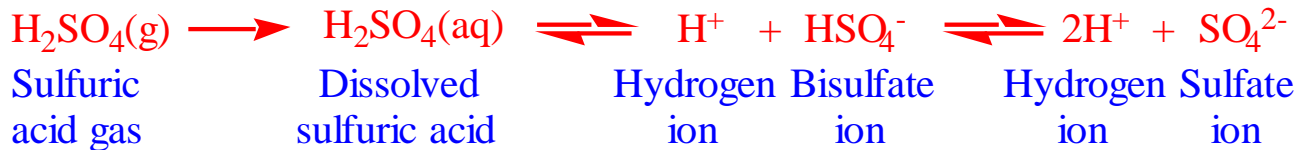
Acid dissociation

Addition of acid to solution increases $[H^+]$, decreasing pH

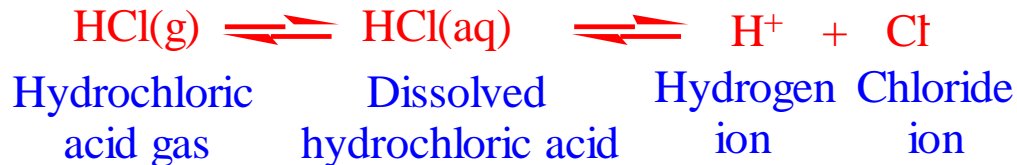
Carbonic acid (gas precursor: CO_2)



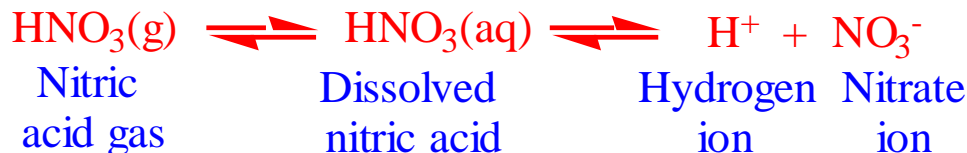
Sulfuric acid (gas precursor: SO_2 , SO_3)



Hydrochloric acid (gas precursor: Cl_2)



Nitric acid (gas precursor: NO , NO_2)



Dry and wet Corrosion

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means.

Dry corrosion

- it involves direct attack of dry gases (air, oxygen, H_2S , SO_2 , etc.) on the metal through chemical reactions. As a result an oxide layer is formed over the surface
- Dry corrosion occurs mainly at high temperatures
- The process is slow

Wet corrosion

- it involves direct attack of aqueous media /strong or dilute (acidic or alkaline) on metal through electrochemical reactions
- The moisture and oxygen are also responsible
- The process is fast