GENERAL CONCEPTS AND FUNDAMENTALS (III)

REACTIONS

Le Chatelier's principle

When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to counteract (partially) the effect of the applied change and a new equilibrium is established.

- ☐ **EFFECT IN CHANGE IN TEMPERATURE.** In exothermic reactions, increase in temperature decreases the equilibrium constant, K, whereas, in endothermic reactions, increase in temperature increases the K value.
- ☐ **EFFECT IN CHANGE IN PRESSURE.** The equilibrium concentrations of the products and reactants do not directly depend on the total pressure of the system. They may depend on the partial pressures of the products and reactants, but if the number of moles of gaseous reactants are equal to number of moles of gaseous products, pressure has no effect on equilibrium.
- ☐ **EFFECT OF CHANGE IN VOLUME.** Changing the volume of the system changes the partial pressures of the products and reactants and can affect the equilibrium concentrations. With a pressure increase due to a decrease in volume, the side of the equilibrium with fewer moles is more favorable and with a pressure decrease due to an increase in volume, the side with more moles is more favorable
- ☐ **EFFECT ADDING AN INERT GAS.** Adding an inert gas into a gas-phase equilibrium at constant volume does not result in a shift. This is because the addition of a non-reactive gas does not change the equilibrium equation, as the inert gas appears on both sides of the chemical reaction equation

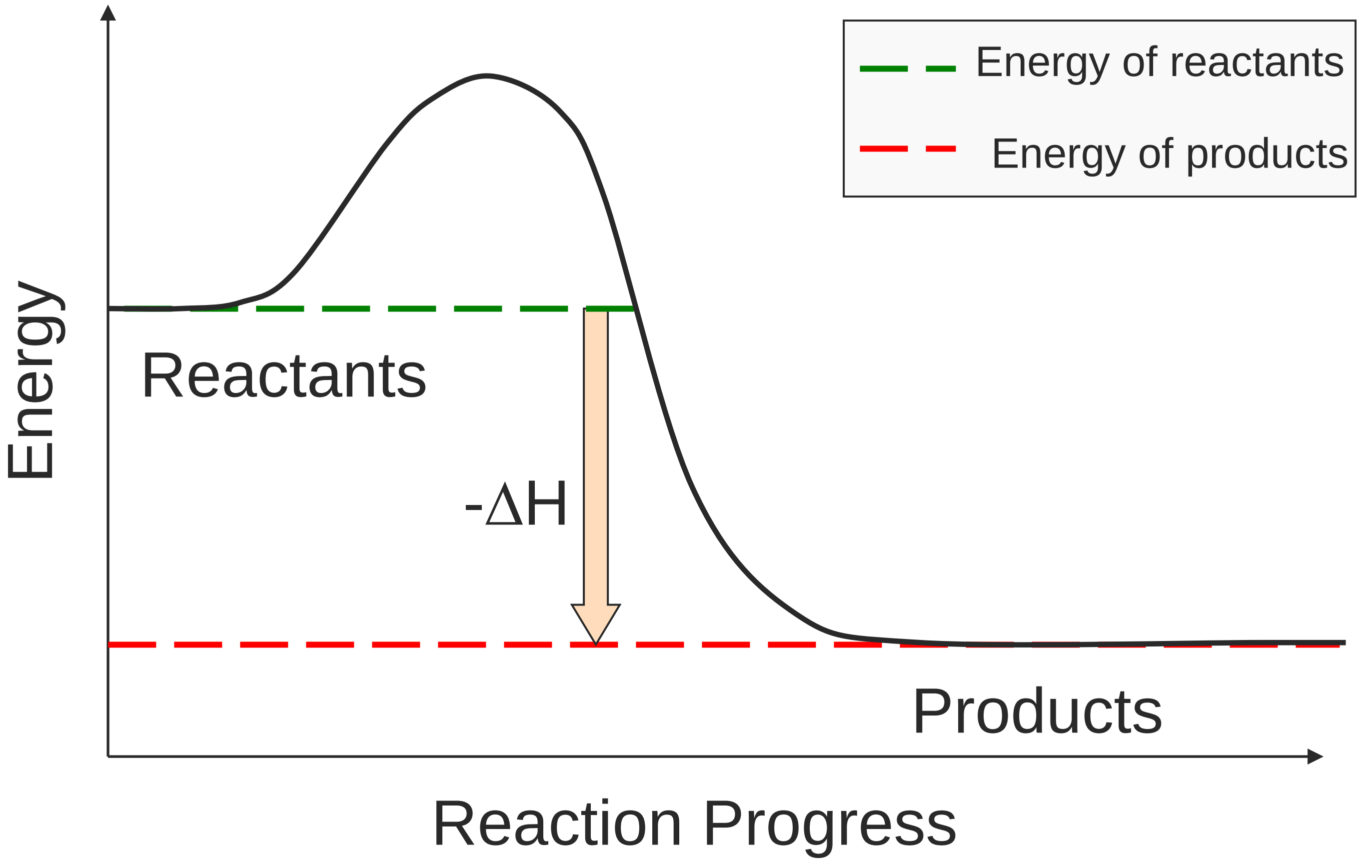
Exothermic Reaction

When the reaction is exothermic (ΔH is negative, puts energy out), heat is included as a product

Reactants $\rightarrow$ Products + Energy

10 energy = 8 energy + 2 energy

$2\ NO\ (g) + O_2\ (g) = 2\ NO_2\ (g)$

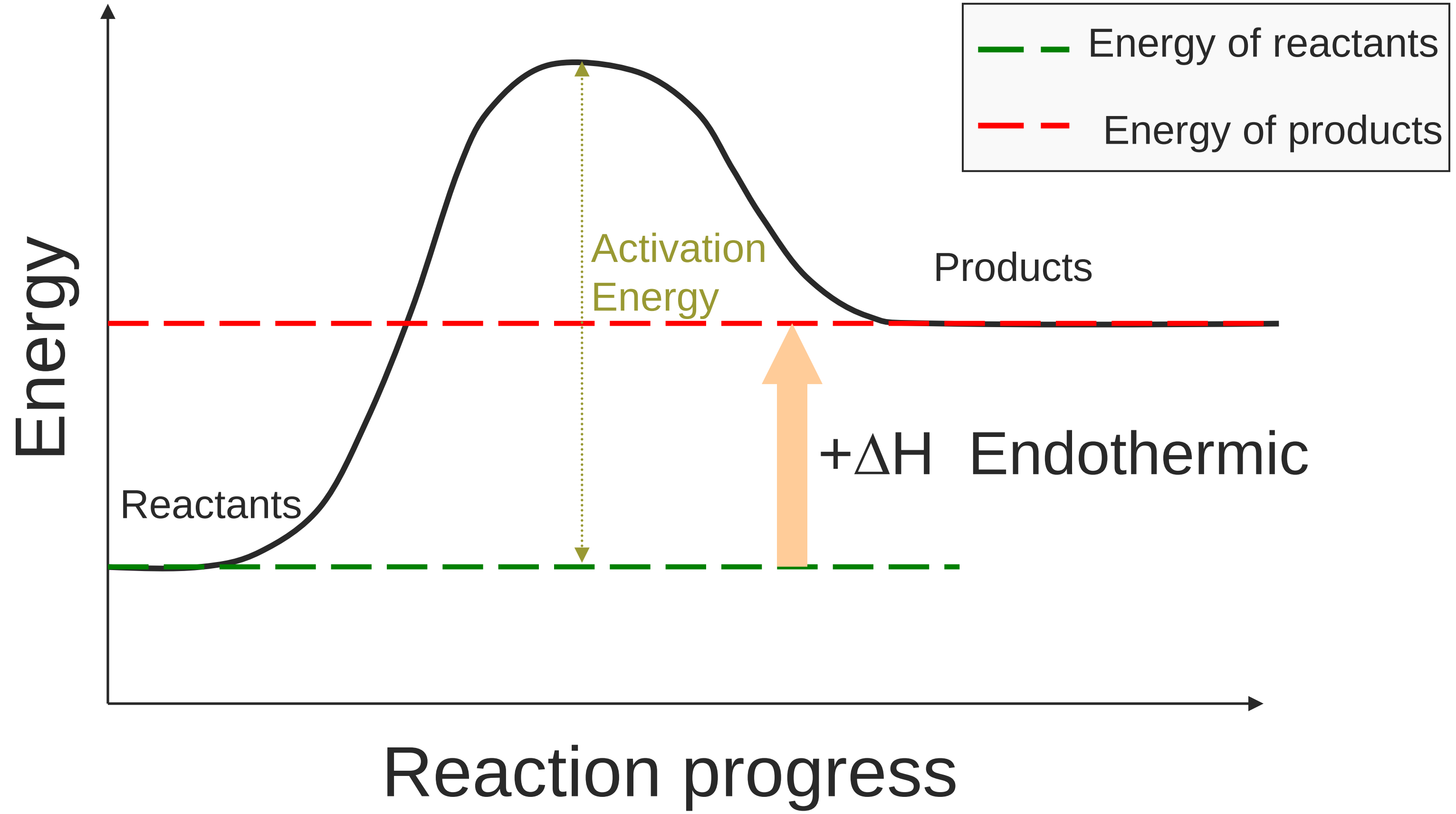


Endothermic Reaction

When the reaction is endothermic (ΔH is positive, takes energy in), heat is included as a reactant.

Energy + Reactants → Products

$N_2(g) + O_2(g) = 2\,NO(g)$



GAS SOLUBILITY: ABSORPTION AND DESORPTION

How can gas solubility be increased ?

$c_{i\ (liq.)} = K_{H(i)} \times p_i$
$K_H \propto 1/T$

Gas solubility can be increased by:

1) increasing the partial pressure of an individual component of a gas mixture
2) decreasing the temperature

1) At constant T, an increase of the partial pressure of an individual component can be obtained

A. at constant total P of the gas mixture, by increasing its molar *(volume)* fraction: $p_i = y_i P$; $y_i = V_i / V$
B. by increasing the total P of the gas mixture: $p_i = y_i P$

2) A decrease of T, other conditions being the same, always leads to an increase of the gas solubility, for all gases.

How can gas solubility be decreased ?

$c_{i\,(liq.)} = K_{H(i)} \times p_i$

$K_H \propto 1/T$

Gas solubility can be decreased by:

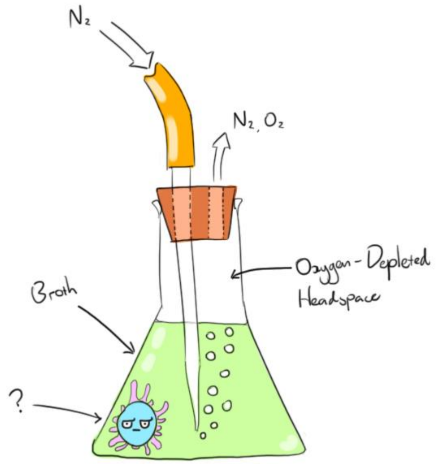
1) decreasing the specific gas component partial pressure
2) increasing the temperature

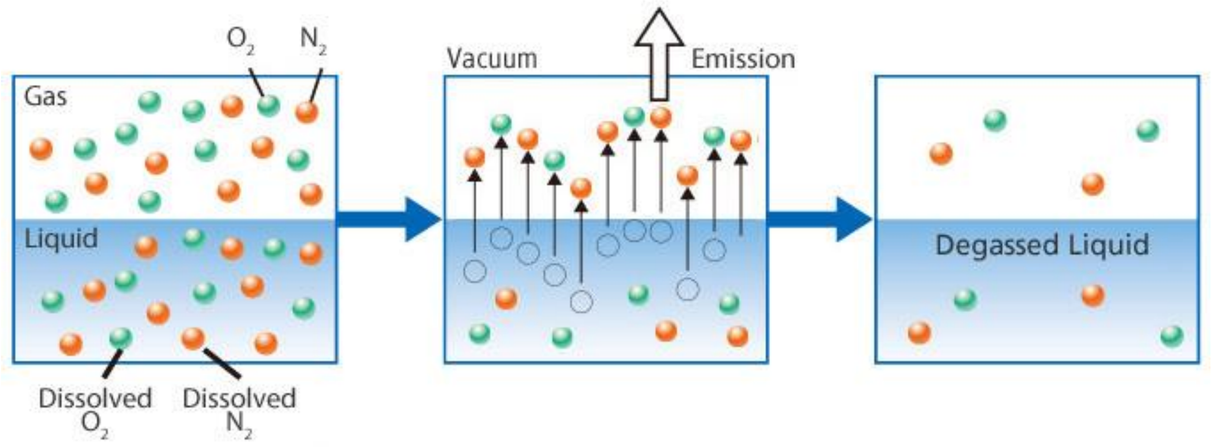
1) At constant T,

- by bubbling an inert gas, e.g. N_2, in the liquid *(below!)*;
- by decreasing the total P of the gas mixture, that is under partial vacuum

Effect of bubbling an inert gas

Effect of a decrease of total P





How can gas solubility be decreased ?

$c_{i\,(liq.)} = K_{H(i)} \times p_i$

$K_H \propto 1/T$

Gas solubility can be decreased by:

1) decreasing the specific gas component partial pressure
2) increasing the temperature

2) Under equilibrium, an increase of T - other conditions being the same - always leads to a decrease of the gas solubility, for all gases.

E.g. boiling the water will strongly decrease the content of all dissolved gases (the pH of water will increase!)

Gas Absorption vs. Gas Desorption

→ WET SCRUBBING vs. GAS STRIPPING!

WE MAY BE INTERESTED IN BOTH PROCESSES.

GAS DESORPTION *(or Volatilisation)*

- **Removal of gaseous components from liquid systems, requires minimization of the gas solubility: $c_{i\ (liq.)} = K_{H(i)} \times p_i$**

- ☐ **Operating at: higher temperatures ($K_H \propto 1/T$); and/or lower p_i**

Examples:

- ☐ ***Air (oxygen) removal from*** *deionized water to produce high T, high P steam, for steam turbines).*
- ☐ **CO_2 removal from water deionization systems (after cationic exchange).**
- ☐ **NH_3 removal from aqueous solutions.**

Highly soluble gas, such as HCl, can only be partially removed from aqueous solutions!

Gas Desorption and gas stripping

DESORPTION is a phenomenon whereby a gas substance is released from a solid or a liquid.

STRIPPING is obtained through either

- ☐ **forced aeration processes, *or***
- ☐ **steam desorption processes.**

See Bref CWW

Brinkmann, T., Giner, G., Hande, S., Serge, Y., Sancho, R., Delgado, L., 2016. Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector.

Henry's Law constants and temperature

$c_{i\,(liq.)} = K_{H(i)} \times p_i$
$K_H \propto 1/T$

Henry's Law constants for some gases at 25 °C.

Gas	K_H [mol/L-atm] *or [M/atm]*
N_2	6.48×10^{-4}
H_2	7.90×10^{-4}
O_2	1.28×10^{-3}
CH_4	1.34×10^{-3}
CO_2	3.38×10^{-2}

↓

HIGHER SOL.

M = molarity, i.e. mol/liter

Note. This k_H can be represented by $k_H^{c,p}$

Let's calculate the maximum solubility of O_2 at 25 °C in water in eq. with the air

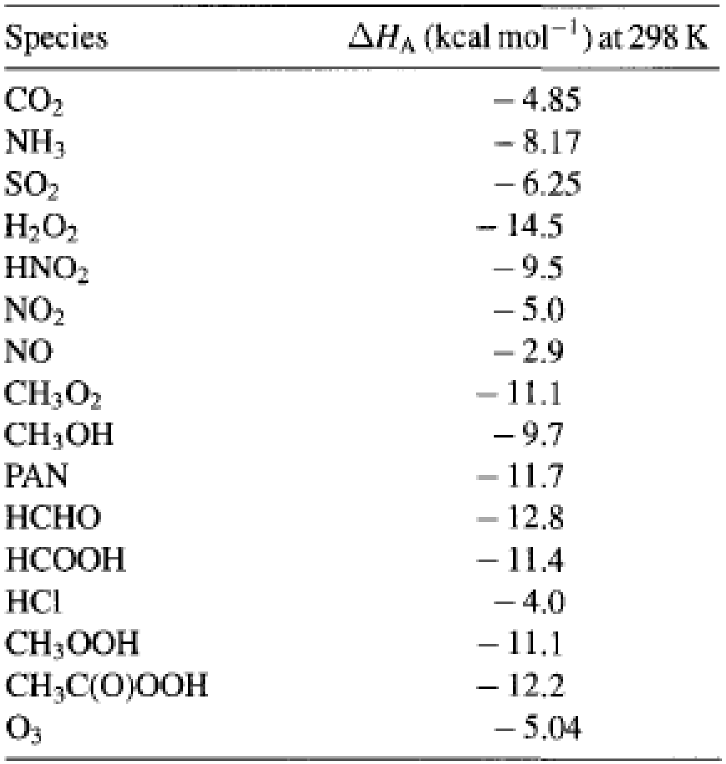
$c_i = K_{Hi}\, p_i = 1.28 \times 10^{-3} \times 0.21 = 0.27$ mmol/L = 0.27 x 32 = ***8.6 mg/L*** *(about 6.6 liters O_2/m^3 of water)*

MW(O_2)=32

Henry's Law constants and temperature: Van’t Hoff equation

$$\ln\left(\frac{K_{H2}}{K_{H1}}\right) = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

Heats are small and negative:
⟶ small intermolecular hydration forces



Species	ΔH_A (kcal mol^{-1}) at 298 K
CO_2	−4.85
NH_3	−8.17
SO_2	−6.25
H_2O_2	−14.5
HNO_2	−9.5
NO_2	−5.0
NO	−2.9
CH_3O_2	−11.1
CH_3OH	−9.7
PAN	−11.7
HCHO	−12.8
HCOOH	−11.4
HCl	−4.0
CH_3OOH	−11.1
$CH_3C(O)OOH$	−12.2
O_3	−5.04

Solute enthalpy of solution for some atmospheric gases

Example.

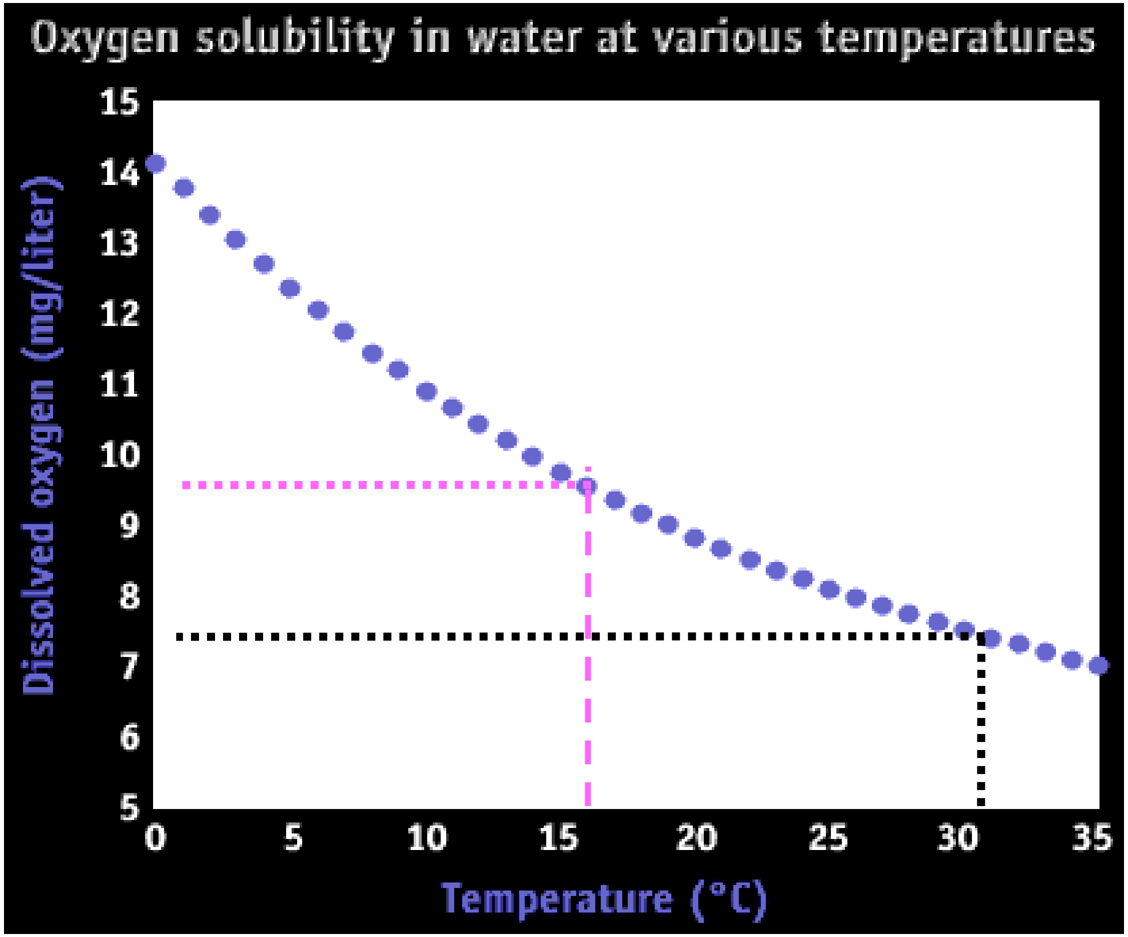
K_{H1} of NH_3 is 90 M/atm at 25 ^{o}C (T_1). Calculate the value of K_{H2} at 50 ^{o}C (T_2).

Ln (K_{H2}/K_{H1}) =-(8170/1.98) x 25/(298 x 323) = -1.072; K_{H2} = 31 M/atm

As expected, the NH_3 solubility decreases.

Henry's Law constants and temperature

Solubility of all gases in liquids *always* decreases when T increases *(e.g. O_2, CO_2 in water)*



Water can become anoxic *(i.e. depleted of dissolved O_2)* at higher temperatures →**in polluted water anaerobic processes occur in summer** with release of CH_4 (biogas) bubbles!.. e.g. FIUME PIOVEGO

Warm water is bad for fishes: [O2] low

Factors Affecting Solubility

Solute-Solvent Interactions

Secondary bonds strength is very important in the absorption/desorption processes:

- **polar compounds tend to dissolve in polar solvents** (e.g. NH_3 gas in water),
- non-polar compounds tend not to dissolve in polar solvents (e.g. N_2 gas in water).

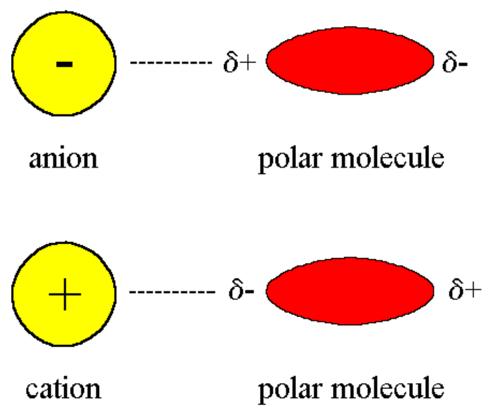
Factors Affecting Aqueous Solubility

Solute-Solvent Interactions:

Ion - dipole > dipole - dipole > non-polar molecules - dipole

Intermolecular forces, particularly dipole-dipole, are important; ions, anyway, are more strongly bound to dipoles: HCl(g) + H_2O = H^+(aq) + Cl^-(aq)

Ion-dipole attractions are stronger than Dipole-Dipole because ions have a larger charge: the bigger the charge, the stronger the attractive force (F = $q^+ q^-$ / $distance^n$)

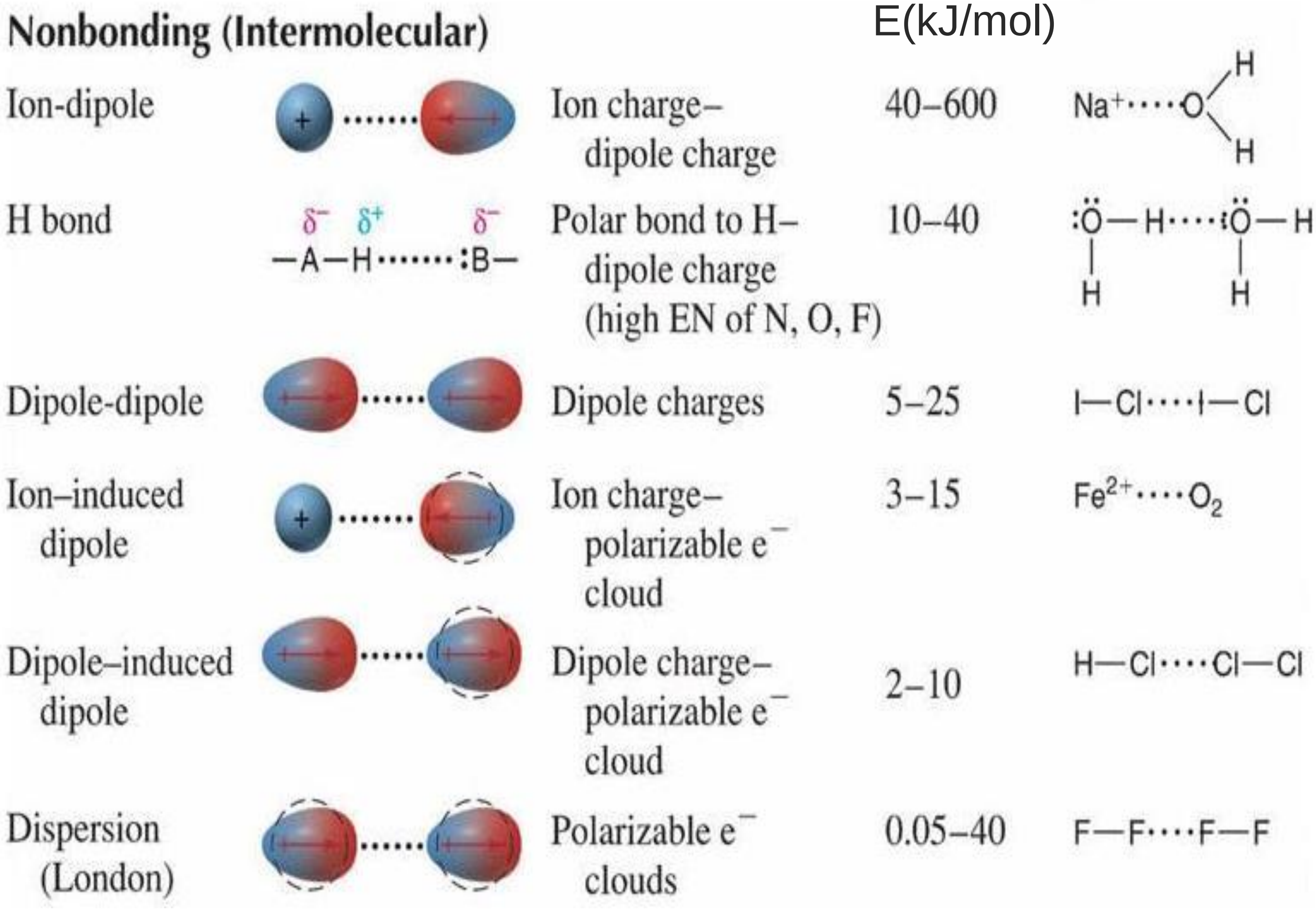


Desorption

Ions are strongly bonded to H_2O molecules and cannot be stripped away.

When boiling tap water, all salts will remain in the water: ion-dipole bonds are too strong to be broken! Only species weakly bonded to water - N_2, O_2, CO_2 + H_2O itself (→ water evaporation) - are stripped away!

Intermolecular Forces (Energy values, kJ/mol)

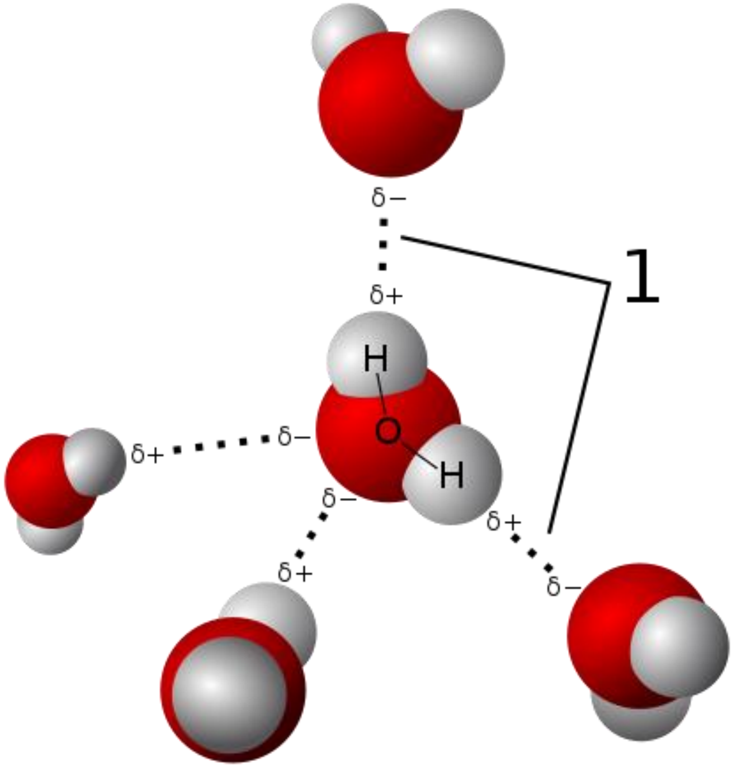


Nonbonding (Intermolecular)			E(kJ/mol)	
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+\cdots OH_2$
H bond	$\overset{\delta^-}{-A}-\overset{\delta^+}{H}\cdots\cdots\overset{\delta^-}{:B}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\ddot{O}(H)-H\cdots:\ddot{O}(H)-H$
Dipole-dipole		Dipole charges	5–25	$I-Cl\cdots I-Cl$
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	$H-Cl\cdots Cl-Cl$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$F-F\cdots F-F$

Hydrogen Bond

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X - particularly the second-row elements nitrogen (N), oxygen (O), or fluorine (F) - is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

Molecules which are capable of hydrogen bonds have hydrogen atoms which are covalently bonded to highly electronegative elements (O, N, F). The presence of hydrogen bonding between molecules of a substance indicates that the **molecules are polar**. This means the molecules will be soluble in a polar solvent such as water



Sweetman, A. M.; Jarvis, S. P.; Sang, Hongqian; Lekkas, I.; Rahe, P.; Wang, Yu; Wang, Jianbo; Champness, N.R.; Kantorovich, L.; Moriarty, P. (2014). "Mapping the force field of a hydrogen-bonded assembly". Nature Communications. 5: 3931. Bibcode:2014NatCo...5E3931S. doi:10.1038/ncomms4931. PMC 4050271. PMID 24875276

What happens to particles of water and to dissolved gas and solids when boiling?

Nothing happens to the water molecules themselves, except that they move faster. Boiling is a physical change, not a chemical one. All that happens is the breaking of weak attractive forces between different **H_2O** molecules: individual H_2O molecules are turned into a vapor (steam).

The same happens to O_2, N_2, CO_2 molecules: the weak attractive forces between O_2, N_2, CO_2 and H_2O molecules are broken and individual molecules are turned into a gas. Gas bubbles float to the surface and escape from liquid water to the atmosphere during heating up.

Dissolved salts are expected to be completely ionized in water e.g. Ca^{2+} and SO_4^{2-}. The strong attractive forces between ions and H_2O molecules are not broken and no individual salt "molecules" are turned into a gas.
If the boiling process is continued, the salts concentrations will increase because of water evaporation.

A SPECIAL CASE

Calcium carbonate ($CaCO_3$) is unusual in that its solubility increases as the temperature of the water decreases.

Carbonate chemistry

Tap and surface waters contain calcium hydrogen carbonate (calcium bicarbonate): Ca^{2+} and HCO_3^-.

$$\underbrace{\overbrace{Ca(HCO_3)_2(aq)}^{Ca^{2+}\text{ and }HCO_3^-}}_{\text{Soluble salt}} \leftrightarrow CO_2(g) + H_2O(l) + \underbrace{CaCO_3(s)}_{\text{Insoluble salt}}.$$

By **heating**, the equil. is shifted to right: $2\ HCO_{3\ (aq)}^- + \text{heat} = CO_{2(g)} + CO_{3\ (aq)}^{2-}$

Because of decreased CO_2 gas solubility at higher temperature *(CO_2 escapes from water)*:

- $HCO_{3\ (aq)}^-$ ions are converted to $CO_{3\ (aq)}^{2-}$ and a fraction of dissolved Ca^{2+} ions form **insoluble** carbonate salts: $Ca^{2+}_{(aq)} + CO_{3\ (aq)}^{2-} = CaCO_{3(s)}$;
- **pH of water slightly increases** due to presence of strong $CO_{3\ (aq)}^{2-}$ base in solution.

In the reverse process, dissolved carbon dioxide (CO_2) in rainwater (H_2O) reacts with limestone calcium carbonate ($CaCO_3$) to form soluble calcium bicarbonate ($Ca(HCO_3)_2$). This soluble compound is then washed away with the rainwater. This form of weathering is called **carbonation**. The pH slightly decreases.

Carbonate chemistry

Calcium hydrogen carbonate (calcium bicarbonate) reacts with calcium hydroxide

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

Calcium hydrogen carbonate reacts with calcium hydroxide to produce calcium carbonate (not soluble) and water.

The chemical method of water softening. Water with high calcium bicarbonate content is often referred to as “hard water” because of the scale it leaves in pipes and sinks.

Thermal decomposition

When heated above 840°C, calcium carbonate decomposes, releasing carbon dioxide gas and leaving behind calcium oxide – a white solid, known as lime

$$CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$$

First, the lime is ‘slaked’ by the water to produce calcium hydroxide (slaked lime)

$$\underset{\text{lime}}{CaO(s)} + \underset{\text{water}}{H_2O(l)} \rightarrow \underset{\text{slaked lime}}{Ca(OH)_2(s)}$$

Gases Reacting with: water / or added chemicals

Gases such as CO_2, SO_2, HCl and NH_3 react with water on dissolution. Chemical reagents are often **added to increase their solubility.**

Example:

- Carbon dioxide dissolves in water and carbonic acid is formed:

$$CO_{2(g)} + H_2O = H_2CO_{3(aq)}$$

- CO_2 dissolves in aqueous NaOH, the product(s) depending on the final pH;

at pH < 9: $CO_{2(g)} + \underbrace{OH^{-}(aq)}_{\text{hydroxide ion}} = \underbrace{HCO_3^{-}{}_{(aq)}}_{\text{bicarbonate ion}}$

An example in class

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

Sodium
hydroxide

Sodium
Carbonate
(soluble salt)

Tavan, Y., Hossein, S., 2017. A novel rate of the reaction between NaOH with CO_2 at low temperature in spray dryer. Petroleum 3, 51–55. https://doi.org/10.1016/j.petlm.2016.11.006

INDUSTRIAL WET SCRUBBING

INDUSTRIAL WET SCRUBBING requires high effective K_H!

WS can be done with plain water, but generally it is added with some chemicals in order to increase the value of: **effective K_H** (thermodynamic effect) and **rate constant, k** (kinetic effect).

High K_H are possible only when strong secondary bonds between the solvent (water) and the dissolved compounds are established:

Strength of sec. bonds: ***Ion-dipole > H bond > dipole-dipole***

Others sec. bonds are too weak for WS!

Some comparisons of intermol. forces:

NH_4^+ -- H_2O (ion-dipole) are stronger than NH_3 -- H_2O (H-bond)

HSO_3^- -- H_2O (ion-dipole) are stronger than SO_2 -- H_2O (dipole-dipole)

Note. Wet scrubbing is designed for the **highest K_H**. Absorption of competitive unwanted species has, however, to be carefully evaluated; ***both thermodynamic*** *and* ***kinetic*** *aspects must be evaluated in Wet Scrubbing!*

pH Effect on Gas Solubility

SO_2 ABSORPTION $SO_2(g) = SO_2(aq)$ H_{so2}

The Henry's Law constant of SO_2 (H_{so2}) *is small (1.2 M atm^{-1} with T=298K). However, the following* ***dissociation*** *processes occur for SO_2 in water:*

$$SO_2(aq) + H_2O = HSO_3^- + H^+ \quad eq_1$$

$$HSO_3^- = SO_3^= + H^+ \quad eq_2$$

The effective Henry's Law constant of SO_2 can be expressed by

$$\mathbf{H_{eff}} = H_{so2} \times \{1 + K_{a1}/[H^+] + K_{a1}\,K_{a2}/[H^+]^2\}$$

The **effective Henry's constant** is strongly dependent on pH.
The values of H_{eff} for **SO_2** under different pH can be calculated by Eq. above:

pH	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
H_{eff} *(M/atm)*	*22*	*$2 \cdot 10^2$*	*$2 \cdot 10^3$*	*$2 \cdot 10^4$*	*$3 \cdot 10^5$*

Exercise 1.10. Absorption of competitive species: SO_2 vs. CO_2

A flue gas contains 44,000 ppm of CO_2 and 300 ppm of SO_2**;** the scrubbing liquor pH is 7. Flue gas stream: 42,500 m^3/h *(= 11.8 m^3/s)*, at 66 ºC. Blow-down: 1.0 m^3/h (liquor discharged).
At pH 7: *$K_{H(CO2)}$ = 0.2 M/atm; $K_{H(SO2)}$* = 3 x 10^5 *M/atm. (Both: H_{eff} !)*

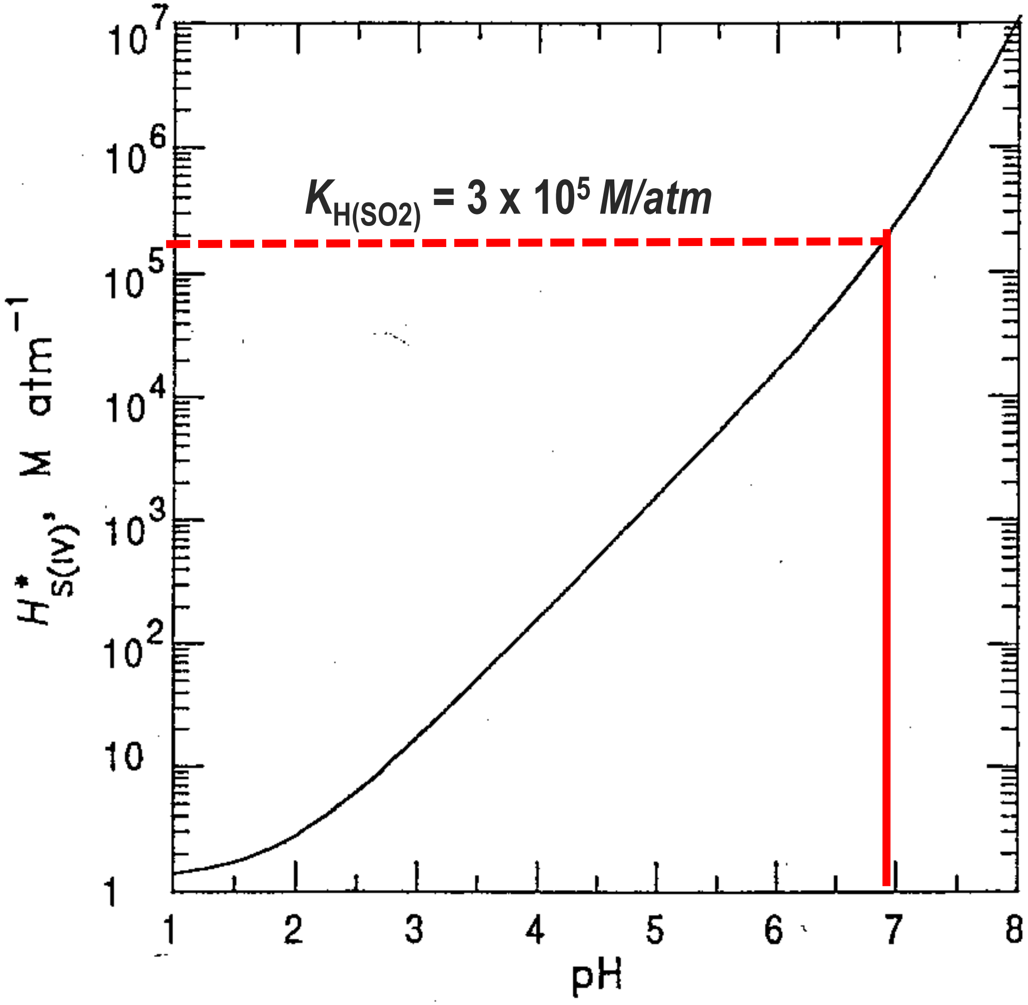
A) Calculate $[CO_2]$aq.;

B) To keep $(SO_2)_g$ < 5 ppm in the cleaned gas, what can be the max SO_2 concentration in the scrubbing liquor?

C) the amount of SO_2 to be removed in mol/h, and kg/h;

D) $[SO_2]$aq in the scrubbing liquor (= blow-down conc.!).

Effective Henry's Law Constant of SO_2 as a Function of pH

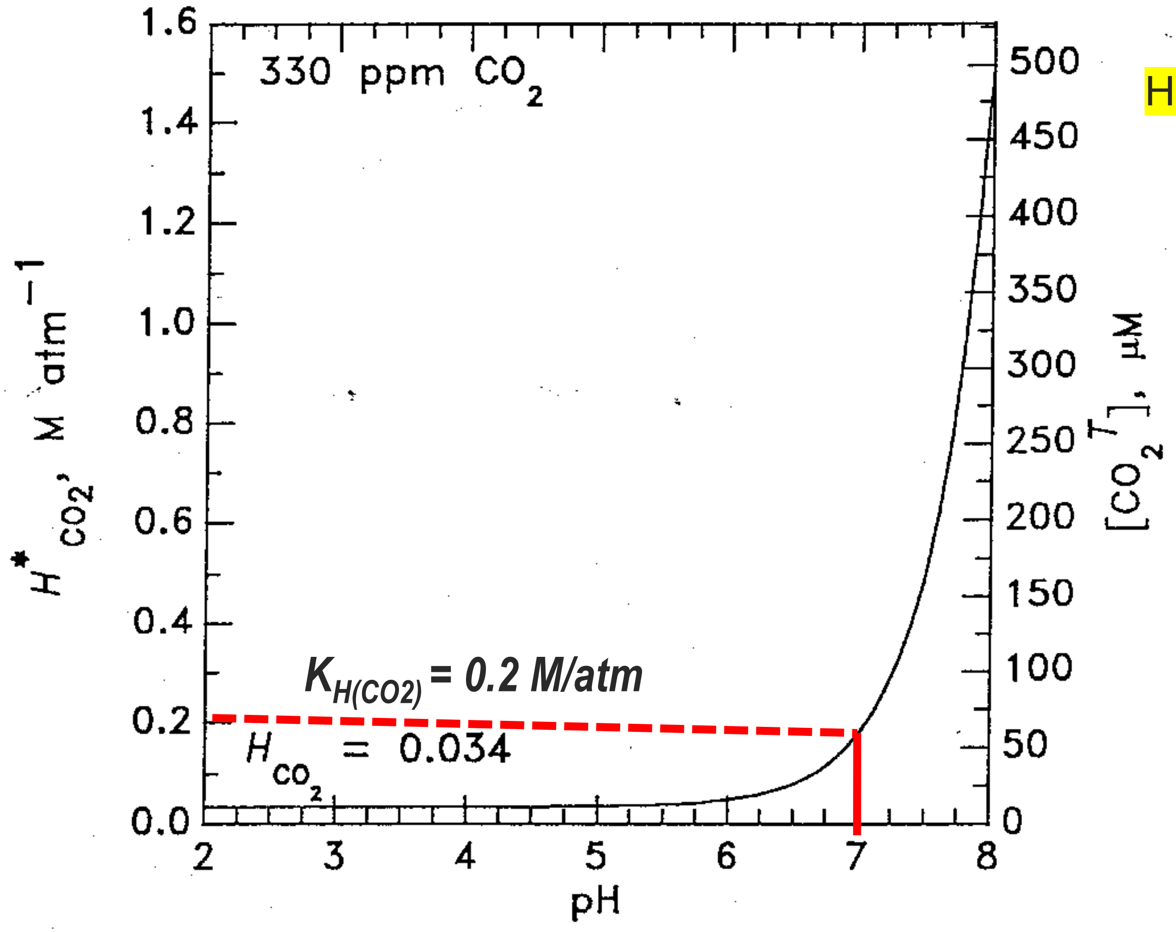


$K_{H(SO2)}$ = 3 x 10^5 *M/atm*

H_{eff} increases with ph

FIGURE 6.6 Effective Henry's law constant for SO_2 as a function of solution pH at 298 K.

Effective Henry's Law Constant of CO_2 as a Function of pH

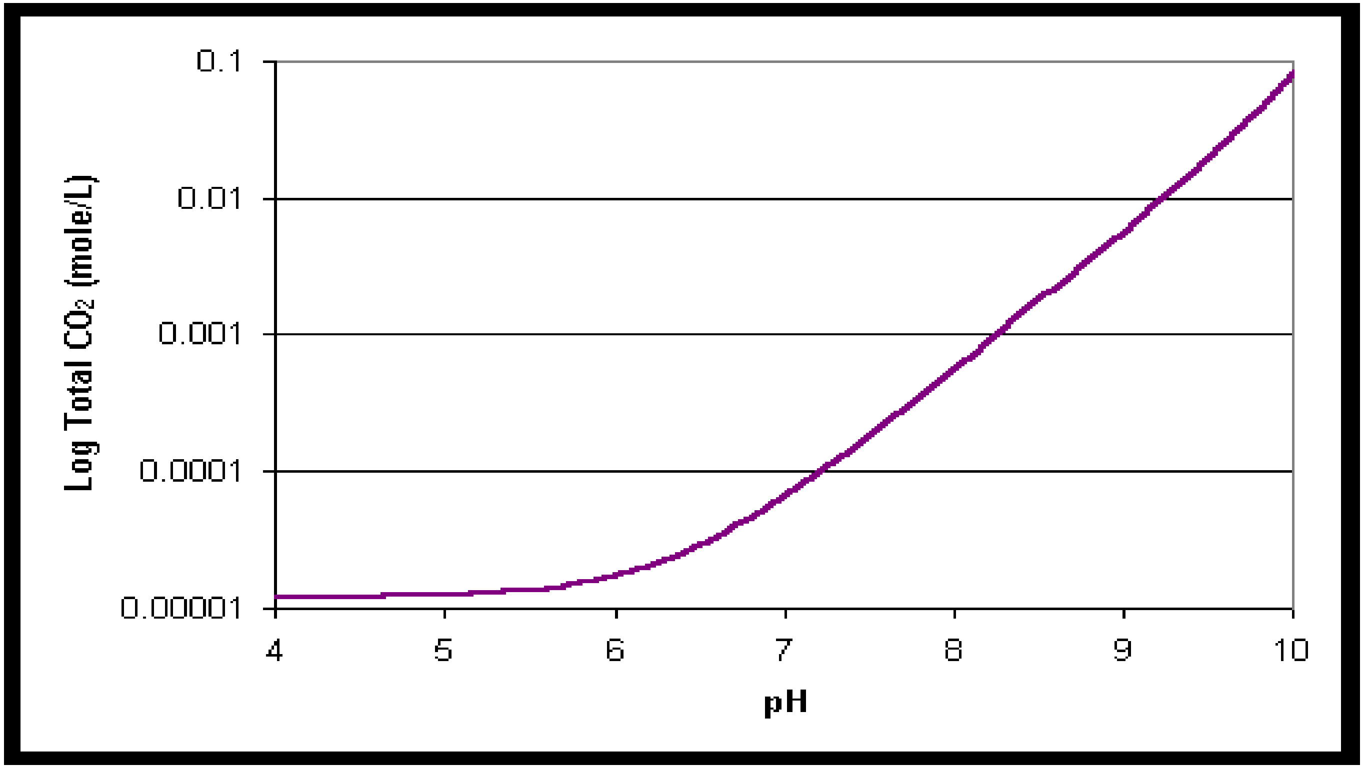


$K_{H(CO2)}$ = 0.2 M/atm

H_{eff} increases with ph

FIGURE 6.4 Effective Henry's law constant for CO_2 as a function of the solution pH. Also shown is the corresponding equilibrium total dissolved CO_2 concentration $[CO_2^T]$ for a CO_2 mixing ratio of 330 ppm.

Effective Henry's Law Constant of CO_2 as a Function of pH



Exercise 1.10. Absorption of competitive species: SO_2 vs. CO_2 - solution

A) *$CO_{2(g)}$=44,000 ppm = 4.4% v/v; $P_{CO2}=x_{CO2}\ P$ =0.044 x 1 = 0.044 atm*

$[CO_2]_{aq} = K_H\ P_{CO2}$

*$[CO_2]_{aq} = 0.2 \times p_{CO2}$ = 0.2 x 0,044 = **8.8 mM** (=0.4 g/L; CO_2 absorbed ≈ 1%)*

B) *$SO_{2(g)}$ = 5 ppm; $\mathbf{P_{SO2}} = x_{SO2} \cdot P = 5 \cdot 10^{-6} \cdot 1 = \mathbf{5.0 \cdot 10^{-6}}$ **atm***

$[SO_2]_{aq}$ in eq. with SO_2 gas 5 ppm = $K_H\ P_{SO2}$

*$[SO_2]_{aq} = 3 \cdot 10^5$ M/atm x $5 \cdot 10^{-6}$ atm = **1.5 M** (max. conc. in solution in eq. with 5 ppm SO_2 in the gas phase)*

C) $SO_{2(g)}$ to be removed: *(300-5) ppm x 42,500 m^3/h = 12.5 m^3/h = 10.1 Nm^3/h = 0.45 kmol/h = 28.8 kg SO_2/h*

D) Concentration of "SO_2" in the liquor:

$[SO_2]_{aq}$ blowdown = Nr moles /Volume = 0.45 kmol/h / 1.0 m^3/h = 0.45 mol/L = ***0.45 M***

Note 1. **The system can really work!** In fact, the concentration of SO_2 in the blow-down liquor is **<** than the maximum conc. permitted by Henry law, that is 1.5 M. **If SO_2 conc. in the blow-down is > than 1.5 M, you cannot reduce the SO_2 conc. down to 5 ppm in the cleaned gas ! The higher the blow-down, the lower the pollutants concentrations in the cleaned gas!**)

Note 2. At pH 7 there is no SO_2 in the aq. phase, but only HSO_3^- (≈70%) and SO_3^{2-} (≈30%) (see Figure in the next slides)

Conclusion: At pH = 7, flue gases can be efficiently desulfurated ,whilst keeping CO_2 absorption at low levels! What about pH 8? What about pH 6?

S(IV) - Mole Fractions as a Function of pH

pH < 2: S(IV) mainly in the form of H_2SO_3(aq)

pH = 2: $[HSO_3^-]/[H_2SO_3(aq)] = 1$

3 < pH < 6: S(IV) mainly in the form of HSO_3^-

pH > 7: S(IV) mainly in the form of SO_3^{2-}

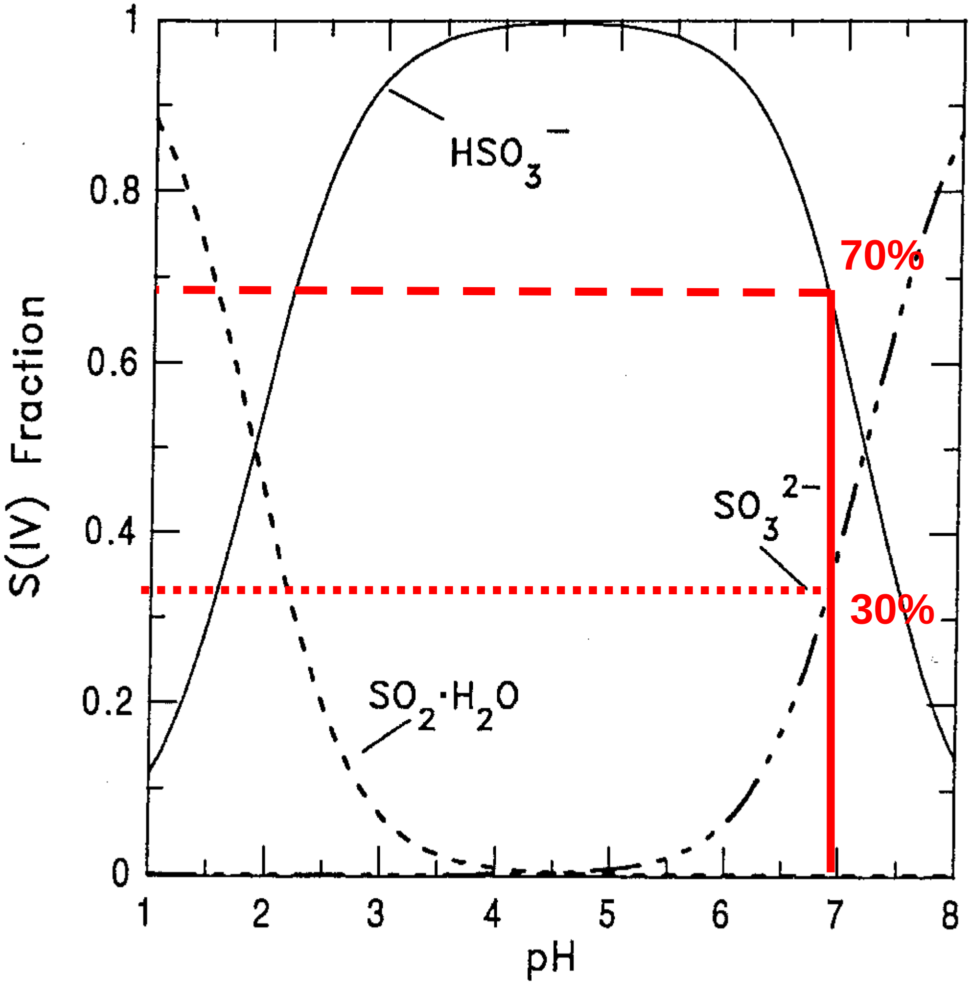
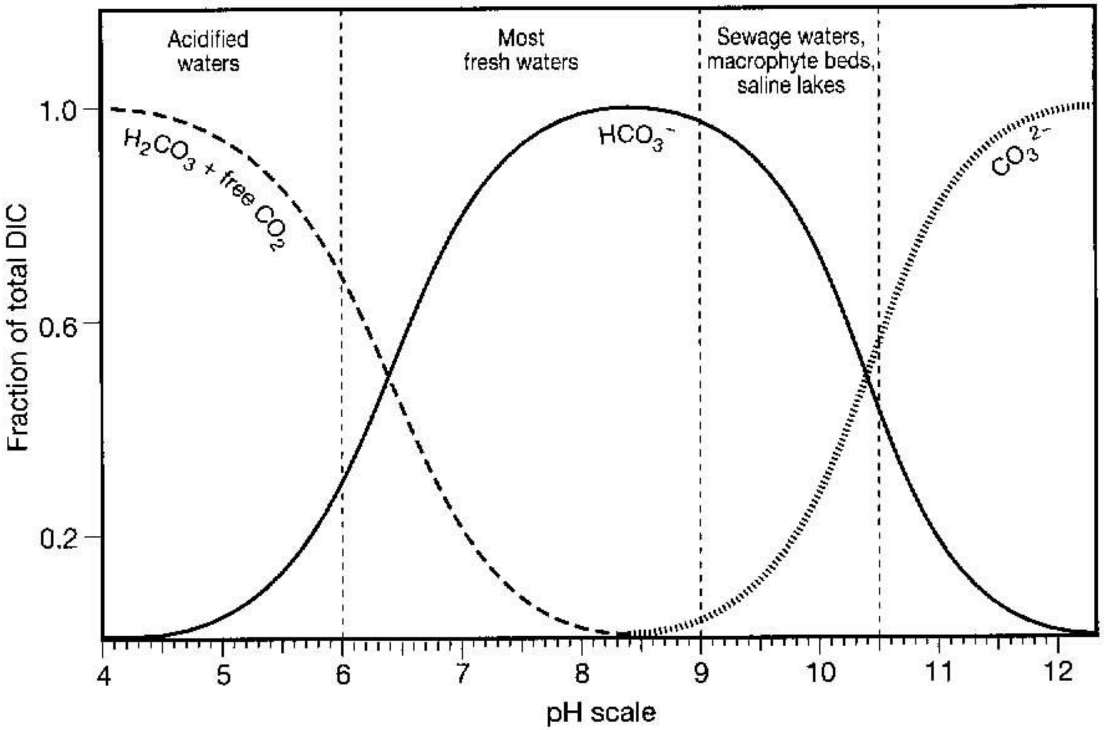


FIGURE 6.8 Concentrations of S(IV) species expressed as S(IV) mole fractions. These fractions are independent of the gas-phase SO_2 concentration.

Which form of carbon will dominate?

DIC = Dissolved Inorganic Carbon

It depends on pH!



pH > 9 should be generally avoided to limit <u>scale formation</u> (mainly $CaCO_3$) and to limit the waste of hydroxide ($NaOH/Ca(OH)_2$) .
High pH are however sometimes required for particular application, e.g. H_2S absorption.

pH > 8 (or better: > 7) should be avoided , when treating flue gases: calcium carbonate and calcium sulfite ($CaSO_3$) scaling will occur in the scrubber, which will result in decreased scrubber efficiency and could even result in shutting down the process to clean the scale formation from the scrubber. If $CaCO_3$ is used as a chemical base (e.g. SO_2 control of coal combustion) pH < 7.

WET SCRUBBING - Examples competitive absorption!

SO_2 vs. CO_2 absorption. What we (should) have learned:

1. *Effective K_H of competitive species should be (much)* ***lower*** *than that of the species to be absorbed ($K_H(CO_2) = 0.2$ M/atm; $K_H(SO_2) = 3 \times 105$ M/atm).*
2. *the competitive effect increases with the ratio, R, of concentrations in the gas phase:* ***R = [competitive species] / [species to be absorbed].***
3. *pH < 7 should be maintained when scrubbing <u>combustion flue gases</u> (power plants, waste incinerators, etc.) (problem of scale formation).*
4. *pH > 7 can be accepted when CO_2 concentration is low (e.g. WS of polluted* ***air****) because $H_{eff,CO2}$ increase with ph and it could be too competitive.*
5. *continuous bleed of the absorbing liquor is required not to increase the concentration of absorbed species up to high values. The bleed rate (or blow-down rate) must be regulated during the performance testing, before normal operation.* ***The lower the bleed-rate, the less efficient will be the scrubber.***
6. *The concentration of the absorbed pollutants in the blow-down must be lower than the calculated eq. values, obtained by application of Henry law.*

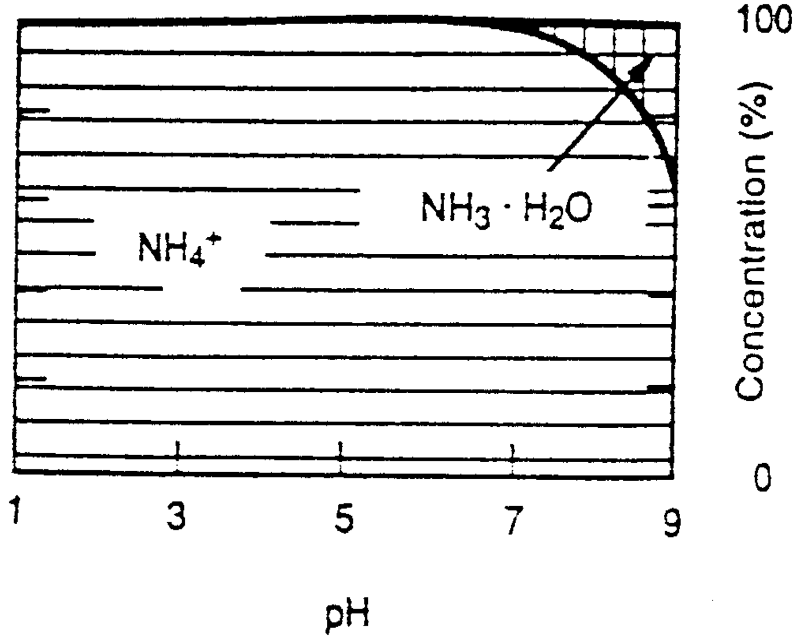
Exercise 1.11. pH of RAIN ACIDIFIED with SO_2

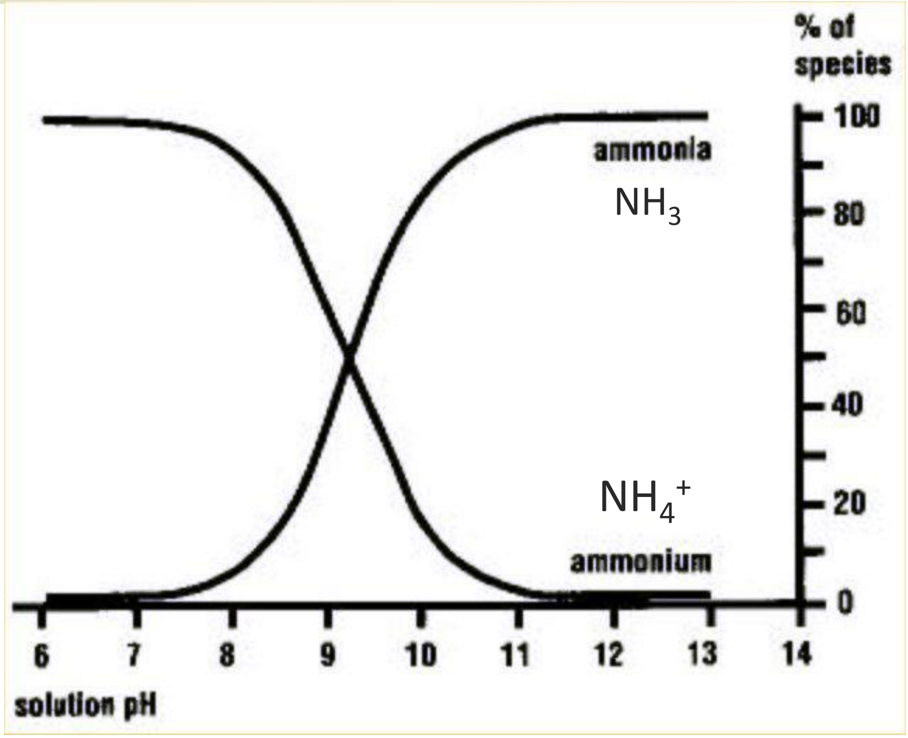
The pH of a rain droplet in equilibrium with an atmosphere with $P_{SO_2}=5 \times 10^{-9}$ atm is 4.85 (*neglect other acids*)

A) What is the concentration of SO_2 in air in *ppm* and *µg/m³* at 20 °C?

pH	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
H_{eff} (M/atm) 20°C	22	$2 \cdot 10^2$	$2 \cdot 10^3$	$2 \cdot 10^4$	$3 \cdot 10^5$

NH_3 Mole Fractions as a Function of pH



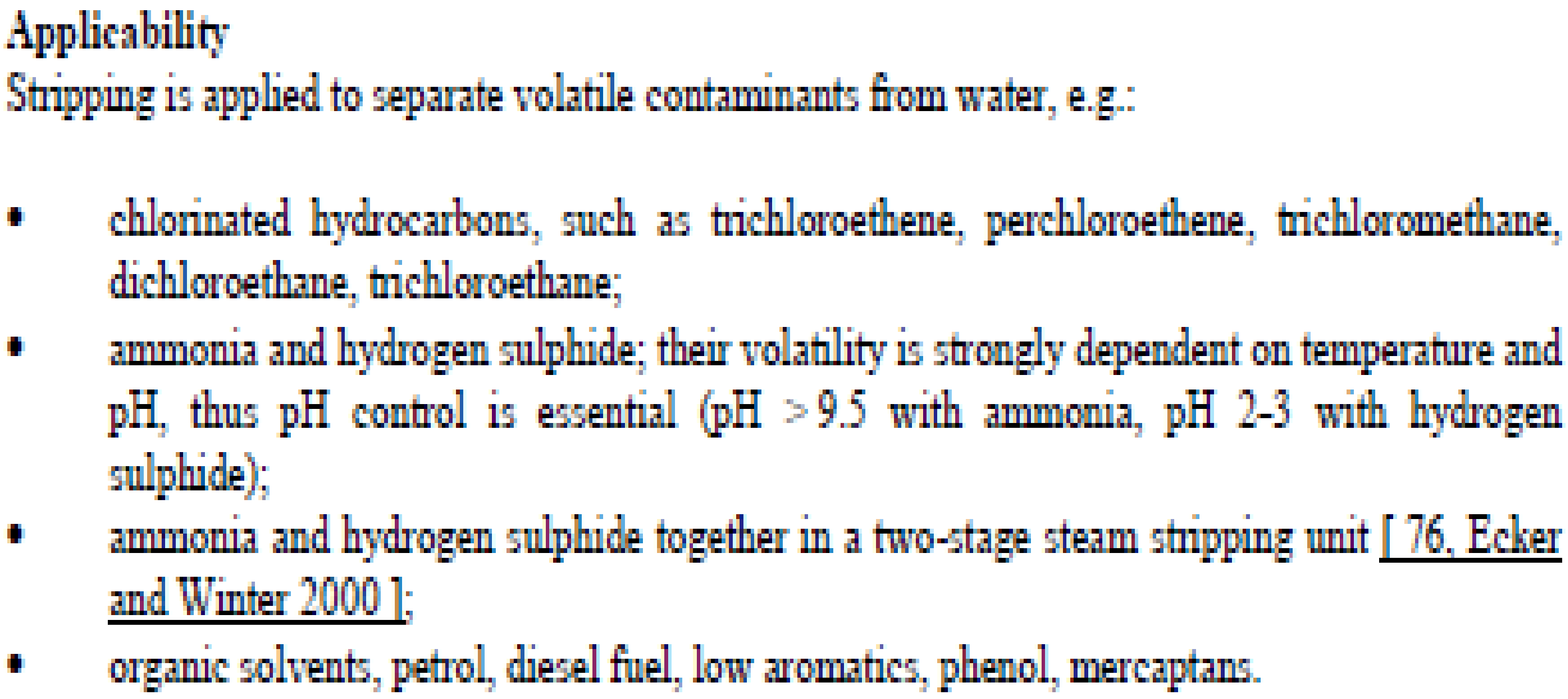


Q_1: Best pH range for NH_3(g) absorption?

Q_2: Best pH range for NH_3(g) stripping from concentrated solutions?

Q_3: What about NH_3(g) stripping from aeration basins of municipal WWTP - waste water treatment plants (pH ≈ 7)?

STRIPPING



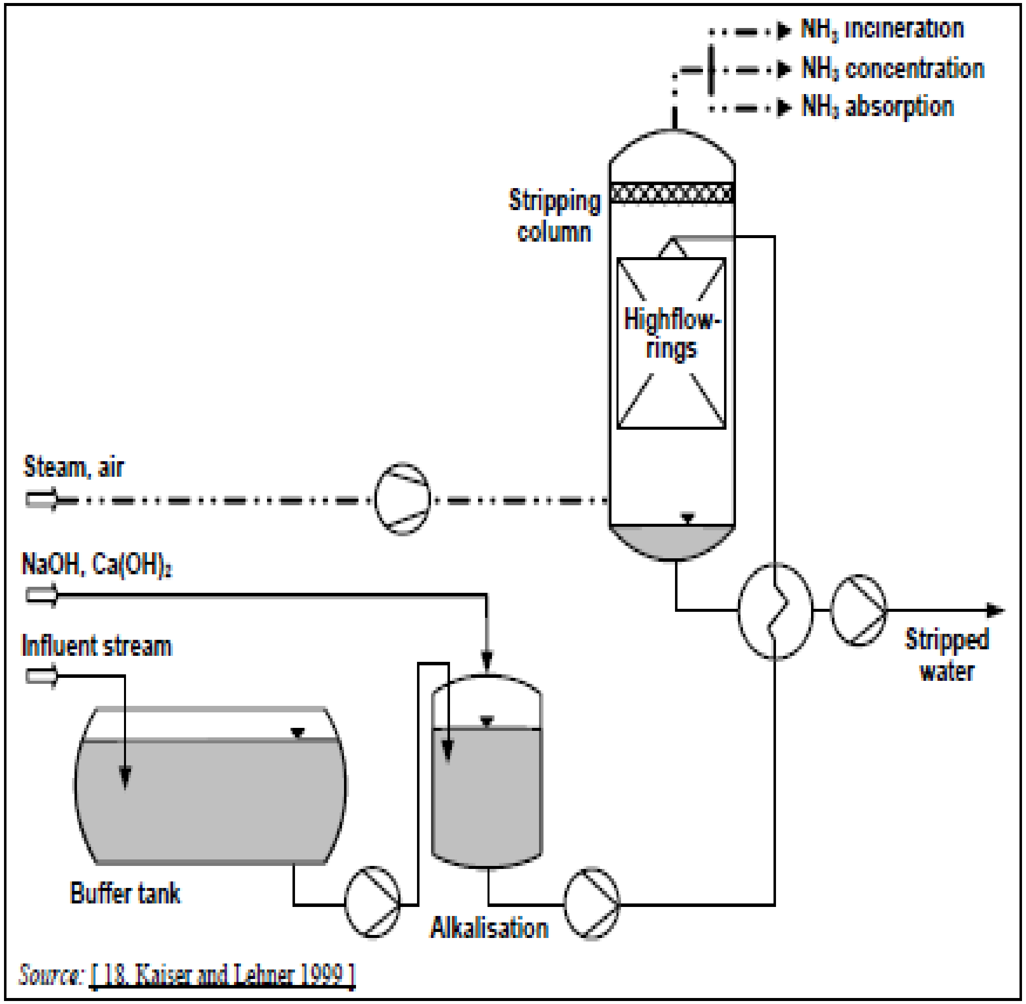
Applicability

Stripping is applied to separate volatile contaminants from water, e.g.:

- chlorinated hydrocarbons, such as trichloroethene, perchloroethene, trichloromethane, dichloroethane, trichloroethane;
- ammonia and hydrogen sulphide; their volatility is strongly dependent on temperature and pH, thus pH control is essential (pH > 9.5 with ammonia, pH 2-3 with hydrogen sulphide);
- ammonia and hydrogen sulphide together in a two-stage steam stripping unit [76, Ecker and Winter 2000];
- organic solvents, petrol, diesel fuel, low aromatics, phenol, mercaptans.

From the CWW Bref (chapter 3)

From the CWW Bref: An example of a stripping process (i.e. the air/steam stripping of ammonia) is illustrated in Figure 3.35.

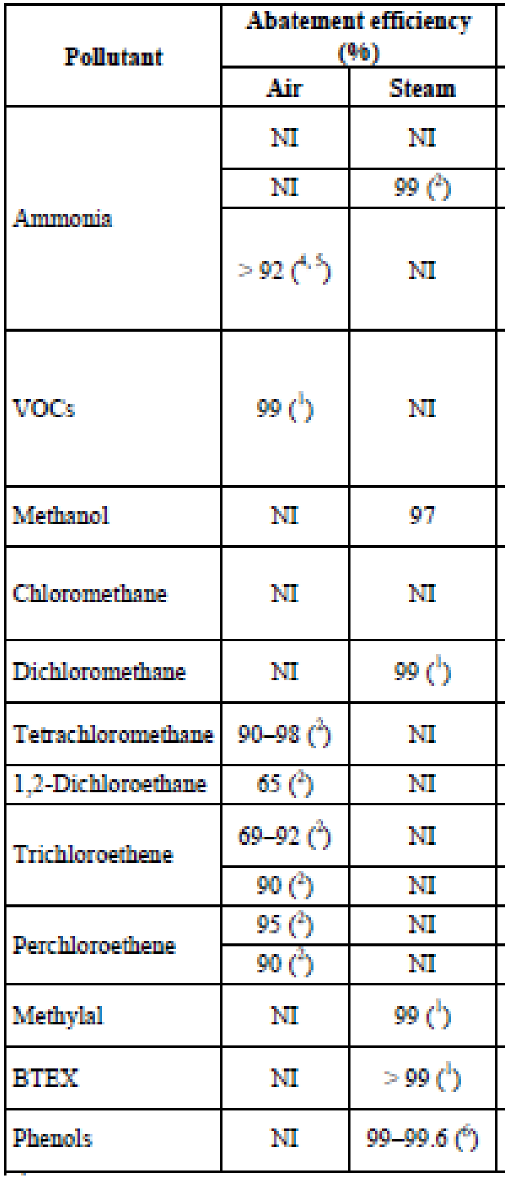


Source: [18, Kaiser and Lehner 1999]

Figure 3.35: Air and steam stripping of ammonia

ABATAMENT EFFICIENCIES AND EMISSION LEVELS ASSOCIATED WITH STRIPPING

From the CWW Bref (Chapter 3 Table 3.97)



Pollutant	Abatement efficiency (%)	
	Air	Steam
Ammonia	NI	NI
	NI	99 (2)
	> 92 (4, 5)	NI
VOCs	99 (1)	NI
Methanol	NI	97
Chloromethane	NI	NI
Dichloromethane	NI	99 (1)
Tetrachloromethane	90–98 (3)	NI
1,2-Dichloroethane	65 (2)	NI
Trichloroethene	69–92 (3)	NI
	90 (2)	NI
Perchloroethene	95 (2)	NI
	90 (3)	NI
Methylal	NI	99 (1)
BTEX	NI	> 99 (1)
Phenols	NI	99–99.6 (6)

Cross-media effects

Stripping is not used as an individual process. It needs at least downstream gas treatment.

The removed VOCs are either recycled to a production process or treated (e.g. by scrubbing, adsorption, thermal or catalytic oxidation). Generally speaking, the treatment of the stripping gas is an essential process step and sometimes more complicated than the stripping operation itself.

To obtain an overall efficient treatment, both the stripping stage and the stripping gas treatment have to be carefully adjusted to each other.

NI: no information provided

STRIPPING: Cross-media effects of waste water and waste gas treatment and their interdependencies

Although waste water treatment systems generally reduce emissions to water, the operation of these systems has its own environmental effect. **Especially relevant with regard to emissions to air from waste water treatment are those water streams which are polluted with volatile organic compounds (VOCs) and volatile inorganic compounds (e.g. ammonia, hydrogen sulphide). Whenever these water flows are open to the atmosphere, (odorous) emissions of these compounds may occur.** Special attention is usually paid to aeration of biological waste water treatment basins, stirring operations, open buffer tanks, settling tanks and waste water stripping facilities. In all of these cases, the emission of pollutants can be shifted from the water compartment to the air. Thus additional waste gas treatment can be necessary. Emissions to air may also evolve from the mixing of water flows with different temperatures or the addition of acids or alkalis for pH adjustment.

The potential impact of waste water treatment plants on the environment is briefly reviewed in Table 1.4.

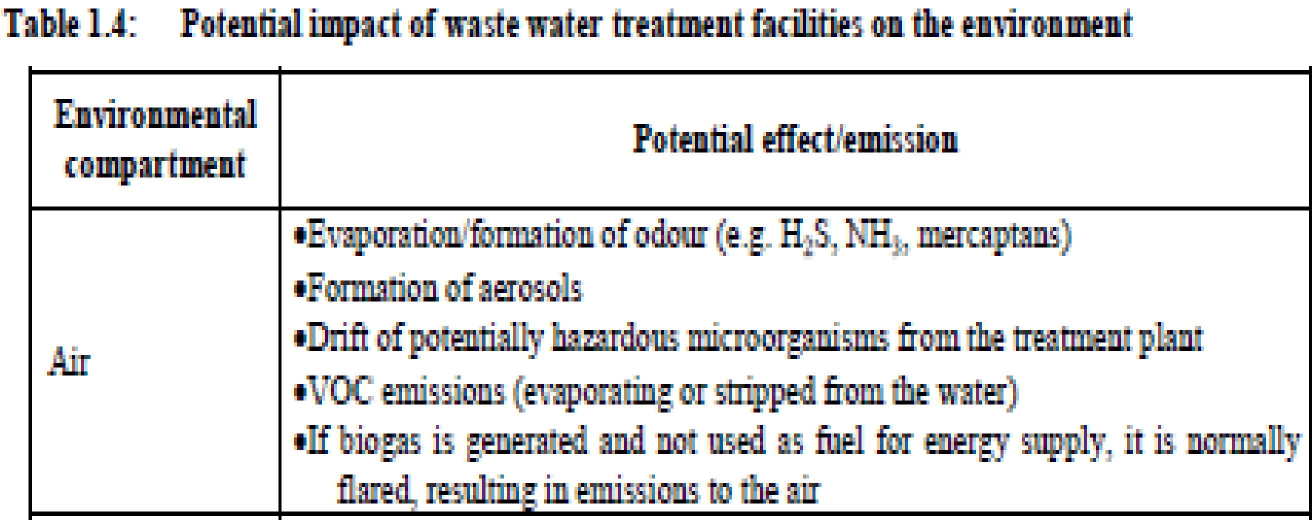


Table 1.4: Potential impact of waste water treatment facilities on the environment

Environmental compartment	Potential effect/emission
Air	•Evaporation/formation of odour (e.g. H_2S, NH_3, mercaptans) •Formation of aerosols •Drift of potentially hazardous microorganisms from the treatment plant •VOC emissions (evaporating or stripped from the water) •If biogas is generated and not used as fuel for energy supply, it is normally flared, resulting in emissions to the air

From the CWW Bref (pag. 36)

“CITTA’ di VERONA” WWTP

WasteWater treatment plant **Città di Verona** – about 300,000 population equivalent

"CITTA' di VERONA" WWTP

Problem.

STRIPPING OF POLLUTANTS FROM A BIOLOGICAL AERATION TANK!

NOT TO BE ACCEPTED!

Solution:

COVERED BASINS -> air extraction → air treatment (WS + Biological Filtration)

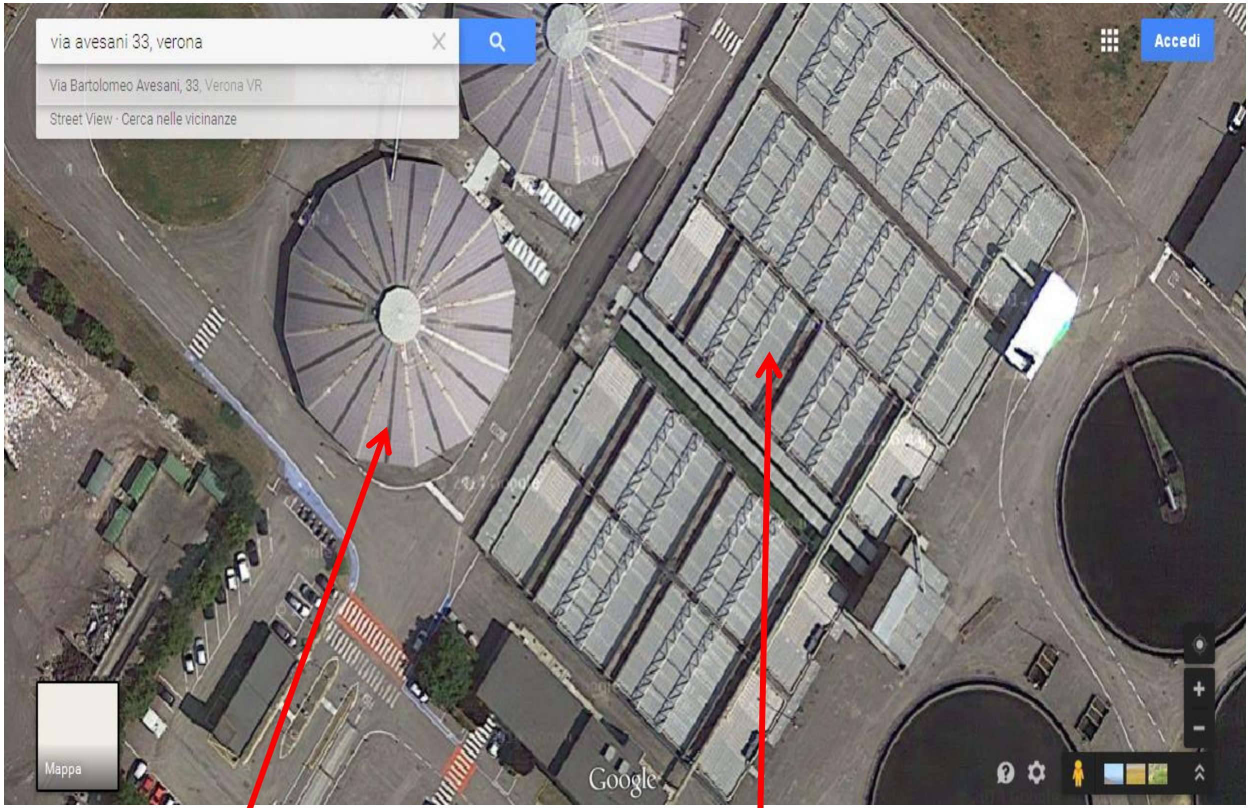
Also: substitution of the surface aeration system (turbine) → «Fine bubble aeration system»

Fine bubble diffuser systems are a key component in controlling economics and environment impact of a wastewater treatment plant.

- ☐ primary sedimentation basins, and
- ☐ aeration basins *(recent installation!)*

completely covered; air is extracted and treated (1st WS + 2nd biofiltration)

“CITTA’ di VERONA” WWTP



Primary sedimentation

Aeration Tanks

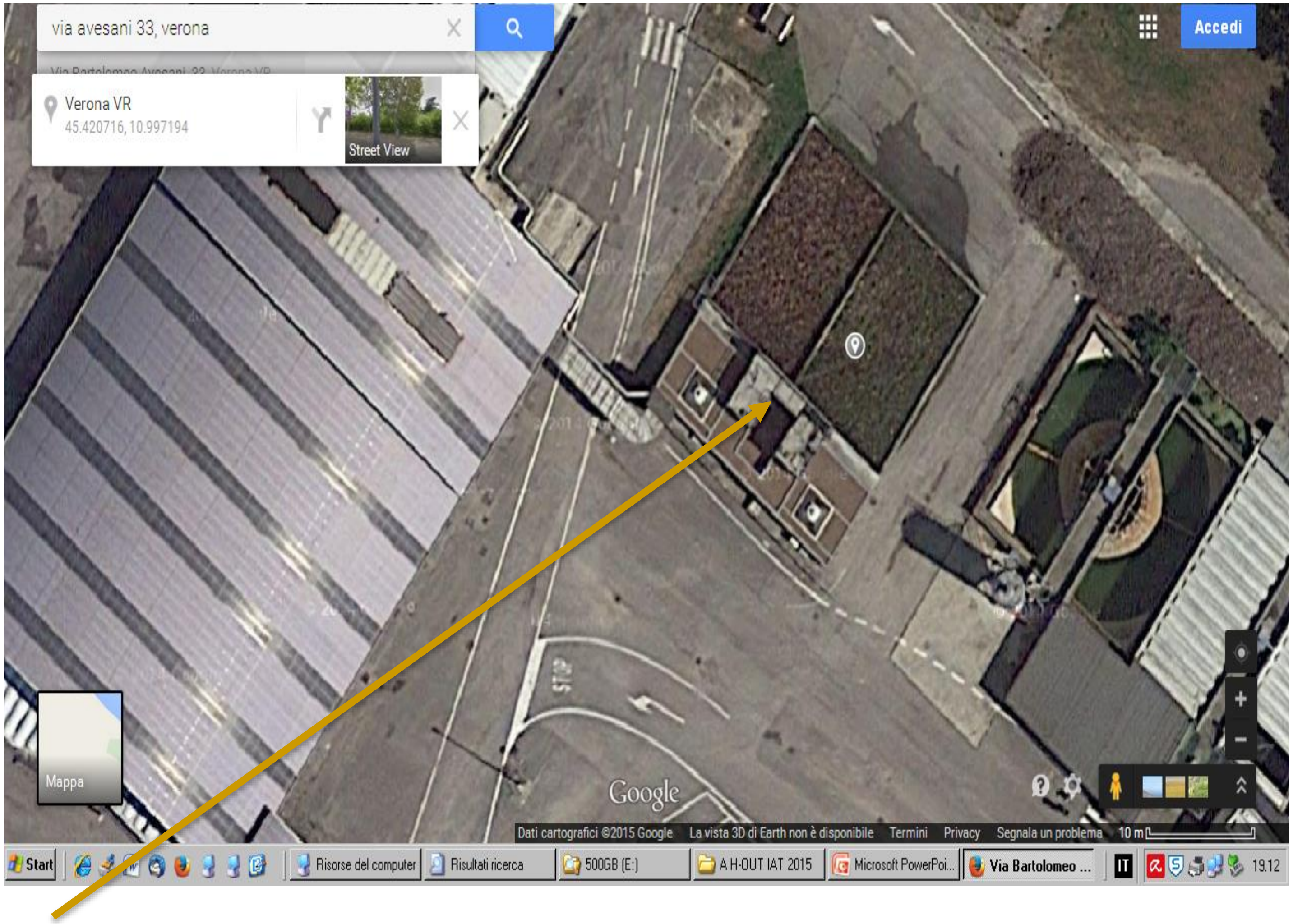
Primary and secondary treatments basins: covered and kept under a constant vacuum; the extracted waste gases is ducted to an odor reduction equipment (Biofilter)

“CITTA’ di VERONA” WWTP

Biological Aeration Basins
Coverage for aeration tanks

3 large primary covered circular sedimentation tanks

“CITTA’ di VERONA” WWTP



via avesani 33, verona

Verona VR
45.420716, 10.997194

Final biofilter for odor control from primary buffer tanks, aeration basins, sludge treatment houses, ..

NEW YORK – NORTH RIVER’S WWTP: odor control

To improve the control of odours from the plant, **New York City** has spent an additional $ 55 million beyond the cost of construction of the original odour control facilities.
North River’s odour control facilities are among the most elaborate in the country.
COMPLETION DATE: 2011

- ☐ **Odour control process**

All the processes are covered except a small portion of the final settling tank, and the air from these processes is collected & vented to the plant's odor control systems prior to being exhausted to atmosphere. Odor treatments:

1. **Wet scrubbing with a mixture of sodium hypochlorite and sodium hydroxide.**
2. **Activated carbon filtration, which absorb odours and chemicals and remove the remaining odour-producing particles.**

The System consists of eight (8) wet scrubbers and twenty-four (24) carbon adsorbers, that will discharge to a common plenum that conveys the treated air to two (2) large exhaust stacks. The maximum exhaust flow rates from are 380,000 m^3/h (per stack).

The air is then released through 30 m tall ventilation stacks.

NEW YORK – NORTH RIVER’S WWTP: odor control

The City of New York constructed a new water pollution control plant on piles and floating concrete platform in the Hudson River to provide primary and secondary wastewater treatment. The roof of the plant was landscaped into a *11 ha*) state park

30 m ventilation stacks on the North River Wastewater Treatment Plant.

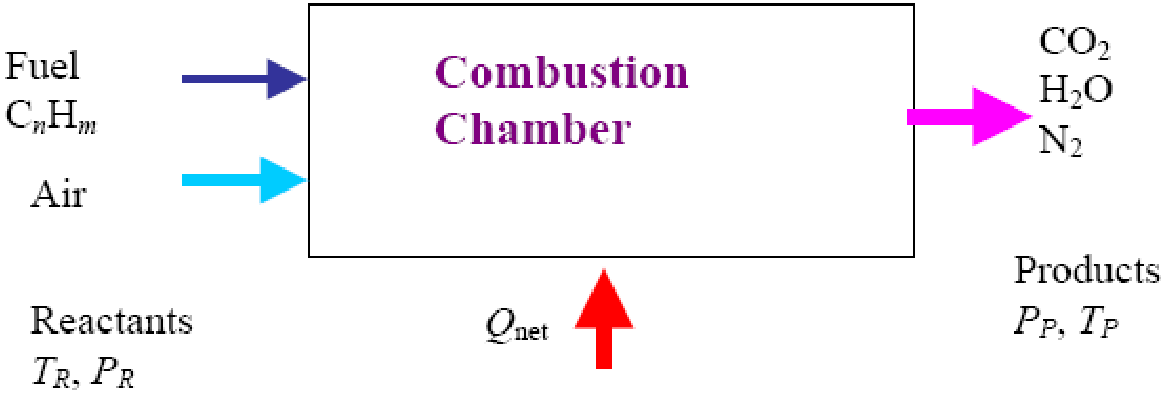
ARZIGNANO’S WWTP: odor control from buffer tanks

5 covered large circular buffer tanks *(50 m diameter):*
extracted air is treated for H_2S WS removal *(LOCAT process)*

COMBUSTION

Combustion process

The combustion process is a chemical reaction whereby fuel is oxidized and energy is released.



Fuel C_nH_m

Air

Combustion Chamber

CO_2 H_2O N_2

Products P_P, T_P

Reactants T_R, P_R

Q_{net}

Fuels are usually composed of some compound or mixture containing carbon, C, and hydrogen, H_2. Examples of hydrocarbon fuels are

- CH_4 Methane
- C_8H_{18} Octane
- Coal Mixture of C, H_2, S, O_2, N_2 and non-combustibles

Initially, we shall consider only those reactions that go to completion. The components prior to the reaction are called reactants and the components after the reaction are called products.

For **complete or stoichiometric combustion**, all carbon is burned to carbon dioxide (CO_2) and all hydrogen is converted into water (H_2O). These two complete combustion reactions are as follows:

$$C + O_2 \rightarrow CO_2$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

Air-Fuel Ratio

Often complete combustion of the fuel will not occur unless there is an **excess of air** present greater than just the theoretical air required for complete combustion.

To determine the amount of excess air supplied for a combustion process, let us define the **air-fuel ratio** *AF* as

$$AF = \frac{kmol\ air}{kmol\ fuel}$$

$$AF = \frac{kg\ air}{kg\ fuel}$$

Percent Theoretical and Percent Excess Air

In most cases, more than theoretical air is supplied to ensure complete combustion and to reduce or eliminate carbon monoxide (CO) from the products of combustion. The amount of excess air is usually expressed as percent theoretical air and percent excess air.

$$\text{Percent theoretical air} = \frac{AF_{actual}}{AF_{th}} 100\% \qquad \text{Percent excess air} = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$

Show that these results may be expressed in terms of the moles of oxygen only as

$$\text{Percent theoretical air} = \frac{N_{O_2\ actual}}{N_{O_2\ th}} 100\% \qquad \text{Percent excess air} = \frac{N_{O_2\ actual} - N_{O_2\ th}}{N_{O_2\ th}} 100\%$$

Some examples to study at home

Example 1. Stechiometric combustion

Example 2. Complete combustion with an excess of air

Example 3. Incomplete combustion with known percent theoretical air

Example 4. Combustion equation when product gas analysis is known

Example 5. Unknown hydrocarbon fuel

Example 1. Octane combustion

A complete combustion of octane in oxygen is represented by the balanced combustion equation. The balanced combustion equation is obtained by making sure we have the same number of atoms of each element on both sides of the equation. That is, we make sure the mass is conserved.

$$C_8H_{18} + A\,O_2 \rightarrow B\,CO_2 + D\,H_2O$$

Note we often can balance the C and H for complete combustion by inspection.

$$C_8H_{18} + A\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O$$

The amount of oxygen is found from the oxygen balance. It is better to **conserve species** on a monatomic basis as shown for the oxygen balance.

$$O: \quad A(2) = 8(2) + 9(1)$$

$$A = 12.5$$

$$C_8H_{18} + 12.5\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O$$

Example 1. Octane combustion

Note: **Mole numbers are not conserved**, but we have conserved the mass on a total basis as well as a specie basis.
The complete combustion process is also called the stoichiometric combustion, and all coefficients are called the stoichiometric coefficients.

In most combustion processes, oxygen is supplied in the form of air rather than pure oxygen.

Air is assumed to be 21 percent oxygen and 79 percent nitrogen on a volume basis. For ideal gas mixtures, percent by volume is equal to percent by moles. Thus, <u>for each mole of oxygen in air, there exists 79/21 = 3.76 moles of nitrogen</u>. Therefore, complete or theoretical combustion of octane with air can be written as

$$C_8H_{18} + 12.5\ (O_2 + 3.76\ N_2) \rightarrow 8\ CO_2 + 9\ H_2O + 47\ N_2$$

Since the total moles of a mixture are equal to the sum of moles of each component, there are 12.5(1 + 3.76) = 59.5 moles of air required for each mole of fuel for the complete combustion process.

Example 1. Octane combustion

The theoretical air-fuel ratio is

$$AF_{th} = \frac{12.5(1+3.76)}{1} = 59.5 \frac{kmol\ air}{kmol\ \ fuel}$$

On a mass basis, the theoretical air-fuel ratio is

$$AF_{th} = 59.5 \frac{kmol\ air}{kmol\ \ fuel} \frac{28.97\ \frac{kg\ air}{kmol\ air}}{[8(12)+18(1)]\frac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 15.12 \frac{kg\ air}{kg\ \ fuel}$$

Example 2. Excess of air

Write the combustion equation for complete combustion of octane with 120 percent theoretical air (20 percent excess air).

$$C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 9\,H_2O + (0.2)(12.5)\,O_2 + 1.2(47)\,N_2$$

Note that (1)(12.5)O_2 is required for complete combustion to produce 8 mol of carbon dioxide and 9 kmol of water; therefore, (0.2)(12.5)O_2 is found as excess oxygen in the products.

$$C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 9\,H_2O + 2.5\,O_2 + 1.2(47)\,N_2$$

Second method to balance the equation for excess air is:

$$C_8H_{18} + 1.2\,A_{th}\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 9\,H_2O + 0.2\,A_{th}\,O_2 + 1.2\,A_{th}(3.76)\,N_2$$

$$O: \quad 1.2\,A_{th}(2) = 8(2) + 9(1) + 0.2\,A_{th}(2)$$
$$A_{th} = 12.5$$

Example 3. Incomplete Combustion with Known Percent Theoretical Air

Consider combustion of C_8H_{18} with 120 % theoretical air where 80 % C in the fuel goes into CO_2.

$$\begin{aligned} &C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\;N_2) \rightarrow \\ &\quad 0.8(8)\;CO_2 + 0.2(8)\;CO + 9\;H_2O + X\;O_2 + 1.2(47)\;N_2 \end{aligned}$$

O balance gives

$$O: \quad 1.2(12.5)(2) = 0.8(8)(2) + 0.2(8)(1) + 9(1) + X\,(2)$$

$$X = 3.3$$

Then the balanced equation is

$$\begin{aligned} &C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\;N_2) \rightarrow \\ &\quad 6.4\;CO_2 + 1.6\;CO + 9\;H_2O + 3.3\;O_2 + 1.2(47)\;N_2 \end{aligned}$$

Example 4. Combustion Equation When Product Gas Analysis Is Known

Propane gas C_3H_8 is reacted with air such that the dry product gases are 11.5 percent CO_2, 2.7 percent O_2, and 0.7 percent CO by volume. What percent theoretical air was supplied?

We assume 100 mol of dry product gases; then the percent by volume can be interpreted to be mole numbers. But we do not know how much fuel and air were supplied or water formed to get the 100 mol of dry product gases.

$$X\ C_3H_8 + A\,(O_2 + 3.76\ N_2) \rightarrow$$
$$11.5\,CO_2 + 0.7\ CO + 2.7\ O_2 + B\ H_2O + A(3.76)\ N_2$$

The unknown coefficients *A*, *B*, and *X* are found by conservation of mass for each species.

$$C:\ \ X(3) = 11.5(1) + 0.7(1) \qquad X = 4.07$$
$$H:\ \ X(8) = B(2) \qquad B = 16.28$$
$$O:\ \ A(2) = 11.5(2) + 0.7(1)$$
$$+ 2.7(2) + B(1) \qquad A = 22.69$$
$$N_2:\ A(3.76) = 85.31$$

Example 4. Combustion Equation When Product Gas Analysis Is Known

The balanced equation is

$$4.07\,C_3H_8 + 22.69\,(O_2 + 3.76\,N_2) \rightarrow$$
$$11.5\,CO_2 + 0.7\,CO + 2.7\,O_2 + 16.28\,H_2O + 85.31\,N_2$$

To simplify this calculation it is generally better to write the combustion equation per mol of fuel. To write the combustion equation per unit mol of fuel, divide by 4.07:

$$C_3H_8 + 5.57\,(O_2 + 3.76\,N_2) \rightarrow$$
$$2.83\,CO_2 + 0.17\,CO + 0.66\,O_2 + 4.0\,H_2O + 20.96\,N_2$$

The theoretical combustion equation is

$$C_3H_8 + 5\,(O_2 + 3.76\,N_2) \rightarrow$$
$$3\,CO_2 + 4.0\,H_2O + 18.80\,N_2$$

Example 4. Combustion Equation When Product Gas Analysis Is Known

The actual air-fuel ratio is

$$AF_{actual} = \frac{(5.57)(1+3.76)kmol\ air\ 28.97\ \frac{kg\ air}{kmol\ air}}{1kmol\ \ fuel[3(12)+8(1)]\frac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 17.45\frac{kg\ air}{kg\ \ fuel}$$

The theoretical air-fuel ratio is

$$AF_{th} = \frac{(5)(1+3.76)kmol\ air\ 28.97\ \frac{kg\ air}{kmol\ air}}{1kmol\ \ fuel[3(12)+8(1)]\frac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 15.66\frac{kg\ air}{kg\ \ fuel}$$

The percent theoretical air is

$$\text{Percent theoretical air} = \frac{AF_{actual}}{AF_{th}}100\%$$

$$= \frac{17.45}{15.66}100 = 111\%$$

Example 4. Combustion Equation When Product Gas Analysis Is Known

or

$$\text{Percent theoretical air} = \frac{N_{O_2\,actual}}{N_{O_2\,th}} 100\%$$

$$= \frac{5.57}{5} 100 = 111\%$$

The percent excess air is

$$\text{Percent excess air} = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$

$$= \frac{17.45 - 15.66}{15.66} 100 = 11\%$$

Example 5. Unknown hydrocarbon fuel

An unknown hydrocarbon fuel, C*X*H*Y* is reacted with air such that the dry product gases are 12.1 percent CO_2, 3.8 percent O_2, and 0.9 percent CO by volume. What is the average makeup of the fuel?

We assume 100 mol of dry product gases; then the percent by volume can be interpreted to be mole numbers. We do not know how much air was supplied or water formed to get the 100 mol of dry product gases, but we assume 1 mol of unknown fuel.

$$C_X H_Y + A\,(O_2 + 3.76\ N_2) \rightarrow$$
$$12.1\,CO_2 + 0.9\ CO + 3.8\ O_2 + B\ H_2O + D\ N_2$$

The five unknown coefficients *A*, *B*, *D*, *X*, and *Y* are found by conservation of mass for each species, *C*, *H*, *O*, and *N* plus one other equation. Here we use the subtraction method for the nitrogen to generate the fifth independent equation for the unknowns.

$$C_X H_Y + A\,(O_2 + 3.76\ N_2) \rightarrow$$
$$12.1\,CO_2 + 0.9\ CO + 3.8\ O_2 + B\ H_2O + D\ N_2$$

Example 5. unknown hydrocarbon fuel

The unknown coefficients *A*, *B*, *D*, *X*, and *Y* are found by conservation of mass for each species. Here we assume the remainder of the dry product gases is nitrogen.

$$N_2:\ D = 100 - (12.1 + 0.9 + 3.8) = 83.2$$

$$O_2:\ A = \frac{D}{3.76} = \frac{83.2}{3.76} = 22.13$$

$$O:\quad A(2) = (12.1)(2) + (0.9)(1) + (3.8)(2) + B(1)$$

$$B = 11.54$$

$$C:\ 1(X) = 12.1(1) + (0.9)(1)$$

$$X = 13.0$$

$$H:\ 1(Y) = B(2)$$

$$Y = 23.08$$

The balanced equation is

$$C_{13}H_{23.08} + 22.13\,(O_2 + 3.76\ N_2) \rightarrow$$

$$12.1\,CO_2 + 0.9\ CO + 3.8\ O_2 + 11.54\ H_2O + 83.2\ N_2$$