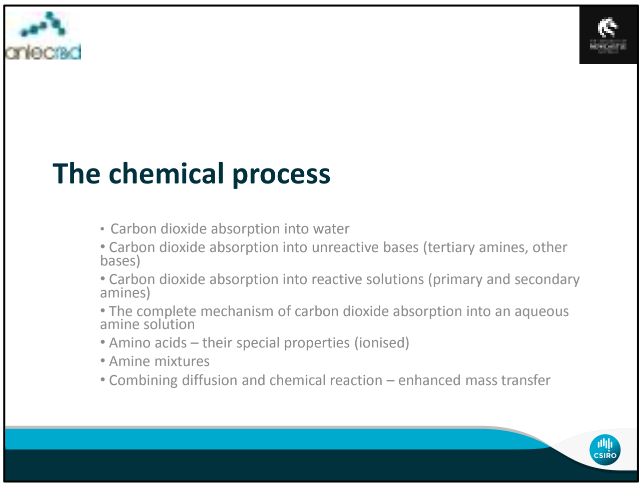
The Chemical Process



The chemical process

- Carbon dioxide absorption into water
- Carbon dioxide absorption into unreactive bases (tertiary amines, other bases)
- Carbon dioxide absorption into reactive solutions (primary and secondary amines)
- The complete mechanism of carbon dioxide absorption into an aqueous amine solution
- Amino acids – their special properties (ionised)
- Amine mixtures
- Combining diffusion and chemical reaction – enhanced mass transfer

Overview of the chemical processes in PCC

There are several parallel processes that occur upon absorption of CO_2 into an aqueous amine solution

CO_2 is transferred from the gas phase into the solution; this is an essentially purely physical process and is to a large extent independent of the amine solution.

Once in solution CO_2 can react with water and hydroxide to form carbonic acid and bicarbonate. These are the only reactions with so-called unreactive bases, such as tertiary amines or carbonate.

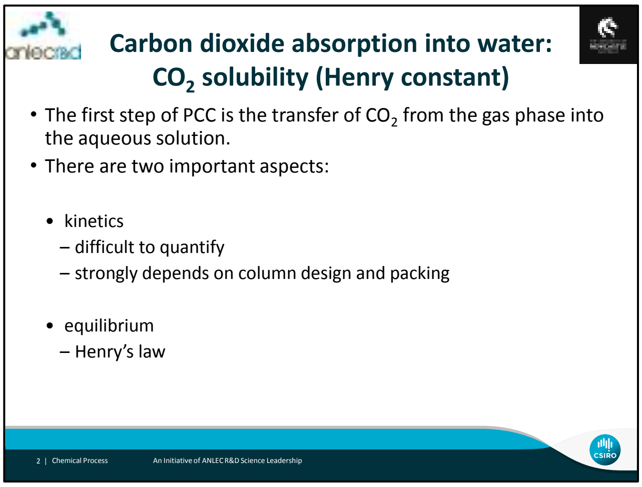
With reactive amines the formation of carbamates occurs parallel and is usually faster than the reactions with water and hydroxide.

Thus the overall reaction mechanism is complex with several reaction paths.

Special amines like di-amines are developed in order to improve the properties relevant for efficient PCC. Very interesting are solutions containing more two or more amine, thus combining the advantages of different amines.

In the end the overall process that includes physical absorption and chemical reactions in solution need to play together as fast and efficient as possible.

CO_2 absorption into aqueous solution



Carbon dioxide absorption into water:
CO_2 solubility (Henry constant)

- The first step of PCC is the transfer of CO_2 from the gas phase into the aqueous solution.
- There are two important aspects:
  - kinetics
    - difficult to quantify
    - strongly depends on column design and packing
  - equilibrium
    - Henry's law

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Solubility of CO_2 in aqueous solution, Henry's constant

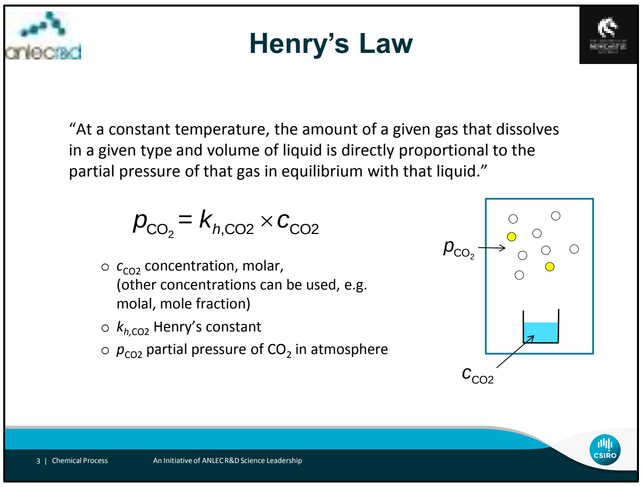
The very first step of the PCC process is the transfer of CO_2 from the gas into the aqueous solution.

There are two aspects that are important: the kinetics and the equilibrium.

The kinetics is difficult to quantify, it strongly depends on the viscosity of the solvent and on the physical shape of the interface surface between the gas and the solution. Column design and appropriate packing are most relevant in improving the kinetics of the process.

The equilibrium situation is much simpler; it is defined by Henry's law.

CO_2 absorption into aqueous solution



Henry's Law

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

$$p_{CO_2} = k_{h,CO2} \times c_{CO2}$$

- c_{CO2} concentration, molar, (other concentrations can be used, e.g. molal, mole fraction)
- $k_{h,CO2}$ Henry's constant
- p_{CO2} partial pressure of CO_2 in atmosphere

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Henry's Law

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

It might be easier to understand the law if written as an equation

$$p_{CO_2} = k_{h,CO2} \times c_{CO2}$$

Where

p_{CO_2} is the partial pressure in the gas phase;

c_{CO2} is the concentration of CO_2 in the solution and

$k_{h,CO2}$ is Henry's constant

This equation represents the equilibrium, the relative concentrations reached after sufficient time. It is easy to reach equilibrium in a closed vessel, such as indicated in the figure; in a PCC absorber equilibrium is probably never really reached.

It is important to remember to use the correct units:

$$k_{h,pc} = \frac{p}{c} = 29.14 \ \frac{\text{L atm}}{\text{mol}}$$

$$k_{h,px} = \frac{p}{x} = 0.163 \times 10^{4} \ \text{atm}$$

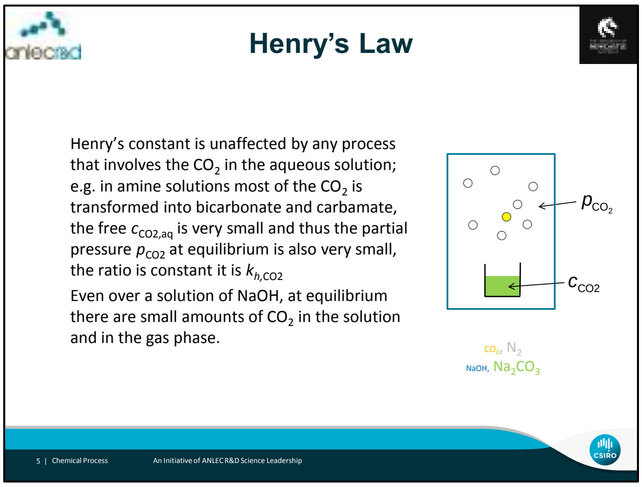
$$k_{h,cc} = \frac{c_{aq}}{c_{gas}} = 0.8317$$

p = partial pressure, in atm

c = concentration, in mol/L

x = mole fraction, dimensionless

CO_2 absorption into aqueous solution



Henry's Law

Henry's constant is unaffected by any process that involves the CO_2 in the aqueous solution; e.g. in amine solutions most of the CO_2 is transformed into bicarbonate and carbamate, the free $c_{CO2,aq}$ is very small and thus the partial pressure p_{CO2} at equilibrium is also very small, the ratio is constant it is $k_{h,CO2}$

Even over a solution of NaOH, at equilibrium there are small amounts of CO_2 in the solution and in the gas phase.

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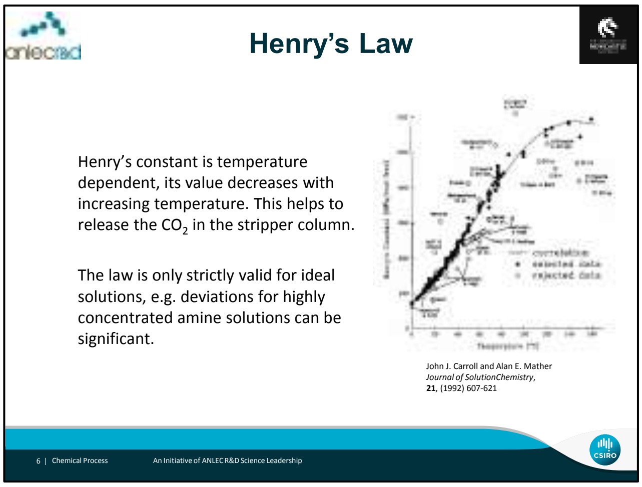
Henry's Law

It is important to realise that Henry's law only applies to the dissolved CO_2 in the liquid phase, not to all the products of the reactions of CO_2 that occur in solution.

In an amine solution most of the CO_2 will be converted into bicarbonate and carbamate, thus the concentration of free CO_2 is very small and as a consequence the partial pressure of CO_2 in the gas phase is also very small. In other words most of the CO_2 is absorbed.

However small the concentrations of CO_2 are in and over an amine solution, once equilibrium is reached the ratio of the two concentrations is the one given by Henry's constant.

CO_2 absorption into aqueous solution



Henry's Law

Henry's constant is temperature dependent, its value decreases with increasing temperature. This helps to release the CO_2 in the stripper column.

The law is only strictly valid for ideal solutions, e.g. deviations for highly concentrated amine solutions can be significant.

John J. Carroll and Alan E. Mather
Journal of SolutionChemistry,
21, (1992) 607-621

6 | Chemical Process

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Henry's Law

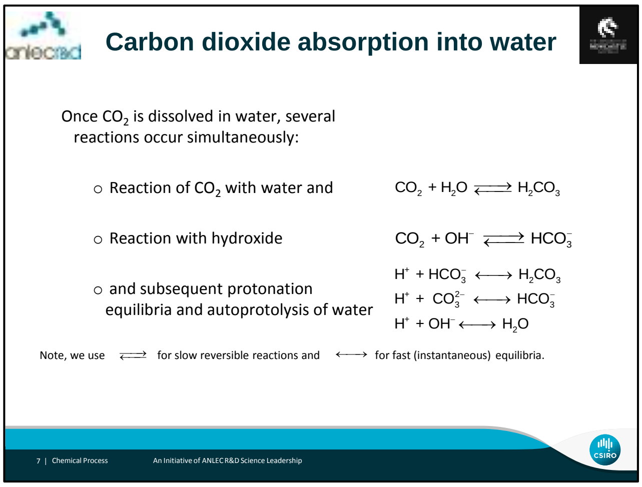
Henry's law describes the ideal case and is strictly valid only for ideal solutions, i.e. at very high dilution. Deviations can be significant for high concentrations, e.g. high concentrations of amine in PCC relevant situations.

Of course Henry's constant is also temperature dependent.

The graph displays published values for the constant as a function of temperature. Note here the partial pressure is expressed as MPa and the concentration in solution as mole fraction.

Most values seem to be consistent but there are also many outliers.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into water

Once CO_2 is dissolved in water, several reactions occur simultaneously:

- ○ Reaction of CO_2 with water and $CO_2 + H_2O \rightleftarrows H_2CO_3$
- ○ Reaction with hydroxide $CO_2 + OH^- \rightleftarrows HCO_3^-$
- ○ and subsequent protonation equilibria and autoprotolysis of water

$$H^+ + HCO_3^- \longleftrightarrow H_2CO_3$$
$$H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$$
$$H^+ + OH^- \longleftrightarrow H_2O$$

Note, we use $\rightleftarrows$ for slow reversible reactions and $\longleftrightarrow$ for fast (instantaneous) equilibria.

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Reactions of CO_2 in basic aqueous solution

CO_2 reacts with water in a reversible reaction to form carbonic acid, H2CO3.

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

CO_2 also reacts in a reversible reaction for from the bicarbonate ion, HCO_3^-.

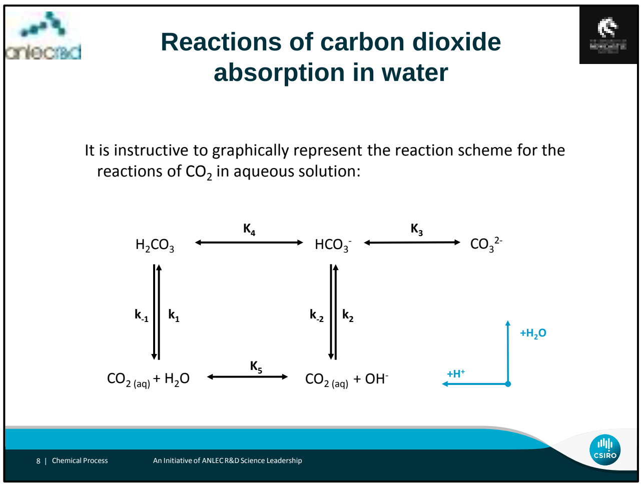
$$CO_2 + OH^- \rightleftarrows HCO_3^-$$

The rate constant for this second reaction is much higher. At high concentration of the hydroxide ions, high pH, the hydroxide path is faster, at low pH the water path is faster. At pH approximately 8.5 both paths are the same. Whatever the pH, both reactions occur simultaneously and only under extreme conditions can one be completely ignored.

In addition to these reactions there are three protonation equilibria. These protonation equilibria establish very fast, much faster that the reactions above, they can be considered instantaneous. (we use the $\longleftrightarrow$ for the protonation equilibria)

$$H^+ + HCO_3^- \longleftrightarrow H_2CO_3$$
$$H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$$
$$H^+ + OH^- \longleftrightarrow H_2O$$

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

It is instructive to graphically represent the reaction scheme for the reactions of CO_2 in aqueous solution:

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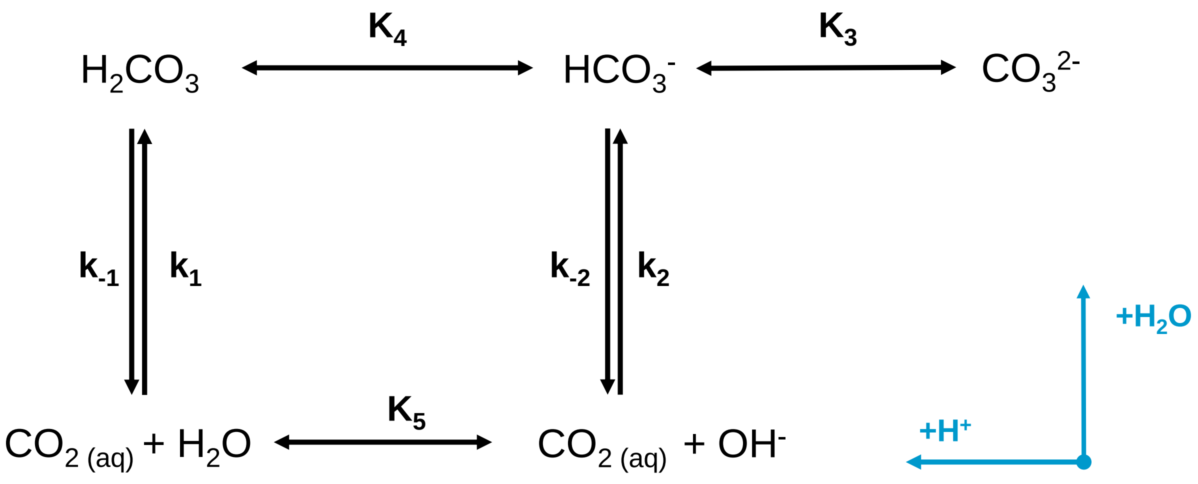
Reactions of CO_2 in basic aqueous solution

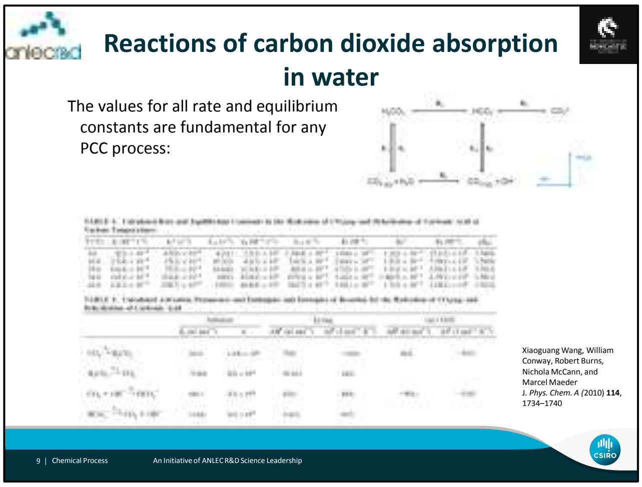
A diagram is probably best to represent the collection of reactions and equilibria that occur parallel in aqueous solution:



The vertical direction indicates reactions of CO_2 with water and hydroxide; the horizontal direction represents the protonation equilibria, the pH.

The diagram represents the interconnectedness of all processes.

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

The values for all rate and equilibrium constants are fundamental for any PCC process:

Xiaoguang Wang, William Conway, Robert Burns, Nichola McCann, and Marcel Maeder
J. Phys. Chem. A (2010) **114**, 1734–1740

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Reactions of CO_2 in basic aqueous solution

Knowledge of the actual values for all rate and equilibrium constants allows complete quantitative understanding of all processes; this includes the time as well as the equilibrium behaviour.

Of course all constants are temperature dependent and this is quantitatively described by Arrhenius, Eyring and van't Hoff relationships:

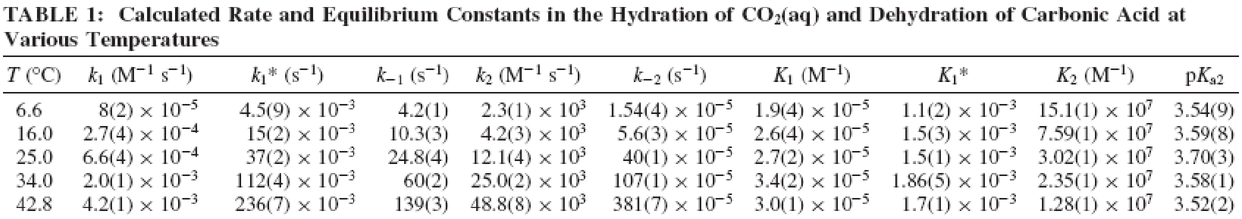


TABLE 1: Calculated Rate and Equilibrium Constants in the Hydration of CO_2(aq) and Dehydration of Carbonic Acid at Various Temperatures

T (°C)	k_1 (M^{-1} s^{-1})	k_1* (s^{-1})	k_{-1} (s^{-1})	k_2 (M^{-1} s^{-1})	k_{-2} (s^{-1})	K_1 (M^{-1})	K_1*	K_2 (M^{-1})	pK_{a2}
6.6	$8(2) \times 10^{-5}$	$4.5(9) \times 10^{-3}$	4.2(1)	$2.3(1) \times 10^{3}$	$1.54(4) \times 10^{-5}$	$1.9(4) \times 10^{-5}$	$1.1(2) \times 10^{-3}$	$15.1(1) \times 10^{7}$	3.54(9)
16.0	$2.7(4) \times 10^{-4}$	$15(2) \times 10^{-3}$	10.3(3)	$4.2(3) \times 10^{3}$	$5.6(3) \times 10^{-5}$	$2.6(4) \times 10^{-5}$	$1.5(3) \times 10^{-3}$	$7.59(1) \times 10^{7}$	3.59(8)
25.0	$6.6(4) \times 10^{-4}$	$37(2) \times 10^{-3}$	24.8(4)	$12.1(4) \times 10^{3}$	$40(1) \times 10^{-5}$	$2.7(2) \times 10^{-5}$	$1.5(1) \times 10^{-3}$	$3.02(1) \times 10^{7}$	3.70(3)
34.0	$2.0(1) \times 10^{-3}$	$112(4) \times 10^{-3}$	60(2)	$25.0(2) \times 10^{3}$	$107(1) \times 10^{-5}$	$3.4(2) \times 10^{-5}$	$1.86(5) \times 10^{-3}$	$2.35(1) \times 10^{7}$	3.58(1)
42.8	$4.2(1) \times 10^{-3}$	$236(7) \times 10^{-3}$	139(3)	$48.8(8) \times 10^{3}$	$381(7) \times 10^{-5}$	$3.0(1) \times 10^{-5}$	$1.7(1) \times 10^{-3}$	$1.28(1) \times 10^{7}$	3.52(2)

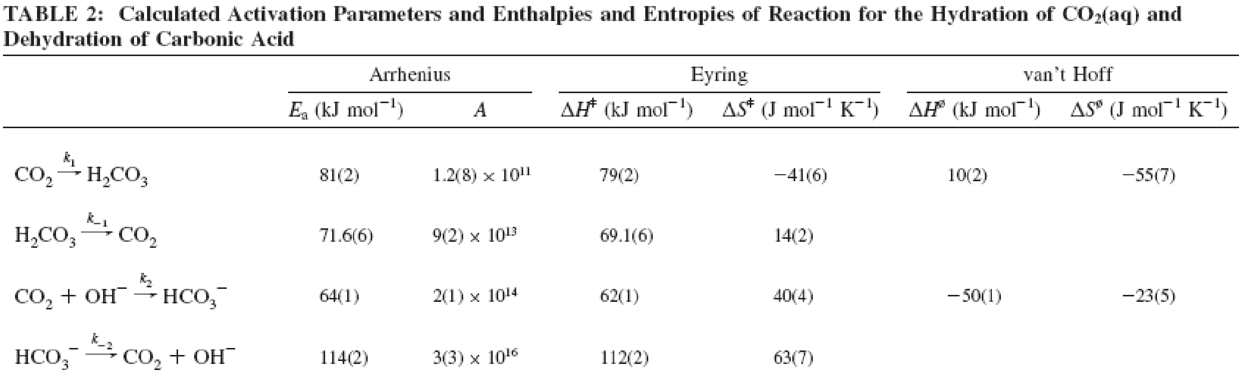
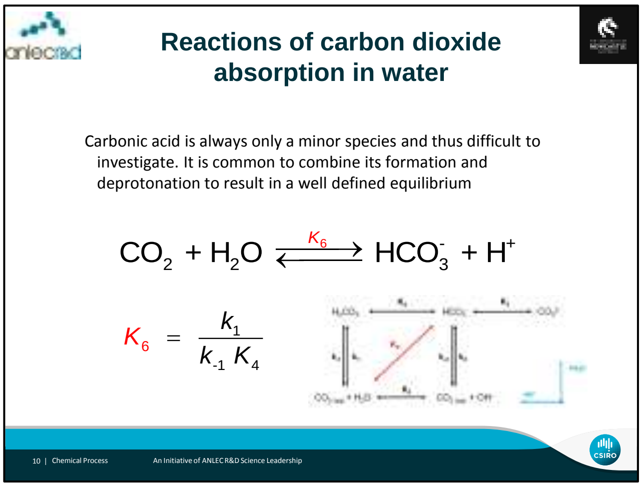


TABLE 2: Calculated Activation Parameters and Enthalpies and Entropies of Reaction for the Hydration of CO_2(aq) and Dehydration of Carbonic Acid

	Arrhenius		Eyring		van't Hoff	
	E_a (kJ mol^{-1})	A	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
$CO_2 \xrightarrow{k_1} H_2CO_3$	81(2)	$1.2(8) \times 10^{11}$	79(2)	−41(6)	10(2)	−55(7)
$H_2CO_3 \xrightarrow{k_{-1}} CO_2$	71.6(6)	$9(2) \times 10^{13}$	69.1(6)	14(2)		
$CO_2 + OH^- \xrightarrow{k_2} HCO_3^-$	64(1)	$2(1) \times 10^{14}$	62(1)	40(4)	−50(1)	−23(5)
$HCO_3^- \xrightarrow{k_{-2}} CO_2 + OH^-$	114(2)	$3(3) \times 10^{16}$	112(2)	63(7)		

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

Carbonic acid is always only a minor species and thus difficult to investigate. It is common to combine its formation and deprotonation to result in a well defined equilibrium

$$CO_2 + H_2O \overset{K_6}{\rightleftarrows} HCO_3^- + H^+$$

$$K_6 = \frac{k_1}{k_{-1} K_4}$$

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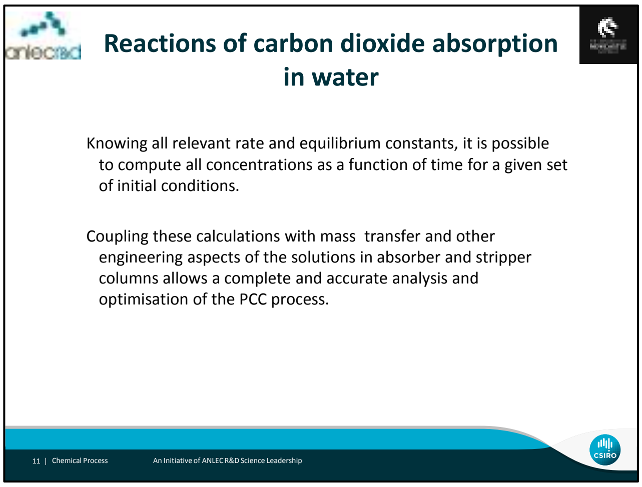
Reactions of CO_2 in basic aqueous solution

Carbonic acid, H_2CO_3, is always only a minor species in aqueous solution, even at low pH the main species is dissolved CO_2(aq), the ration is about 1:1000 at 25 °C.

For this reason it is common to take a ‘shortcut’ from CO_2 directly to the bicarbonate and define a combined equilibrium constant:

$$K_6 = \frac{k_1}{k_{-1} K_4}$$

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

Knowing all relevant rate and equilibrium constants, it is possible to compute all concentrations as a function of time for a given set of initial conditions.

Coupling these calculations with mass transfer and other engineering aspects of the solutions in absorber and stripper columns allows a complete and accurate analysis and optimisation of the PCC process.

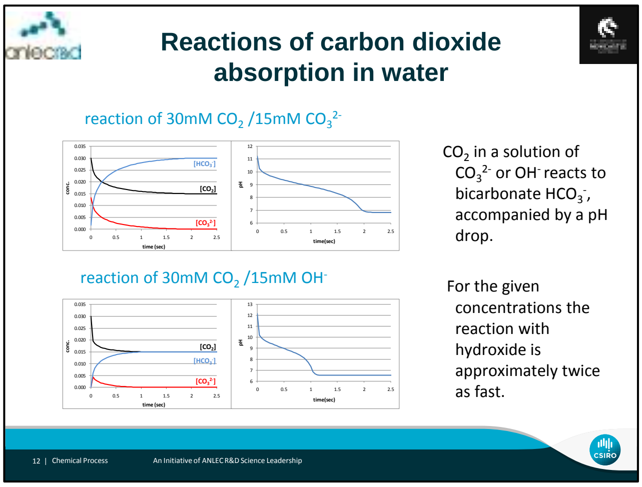
Reactions of CO_2 in basic aqueous solution

The reactions of CO_2 with water and hydroxide are of fundamental importance as they will occur in any PCC application based on aqueous solution. With non-reactive amines they are the only reactions, with reactive amines they occur parallel with the carbamate forming reactions.

The more detailed the knowledge about all aspects of the chemical reactions that occur during PCC processes, the more reliable the processes can be modelled and understood.

Maybe more importantly, the quantitative understanding of the PCC processes allow the rational development of improvements. It is the collaboration between scientists)who investigate the processes on a molecular/test tube level) and chemical engineers (who apply the chemistry in industrial size situations) that will result in the step-wise development of more efficient PCC processes.

Reactions of CO_2 with H_2O and OH^-



Reactions of carbon dioxide absorption in water

reaction of 30mM CO_2 /15mM CO_3^{2-}

CO_2 in a solution of CO_3^{2-} or OH^- reacts to bicarbonate HCO_3^-, accompanied by a pH drop.

reaction of 30mM CO_2 /15mM OH^-

For the given concentrations the reaction with hydroxide is approximately twice as fast.

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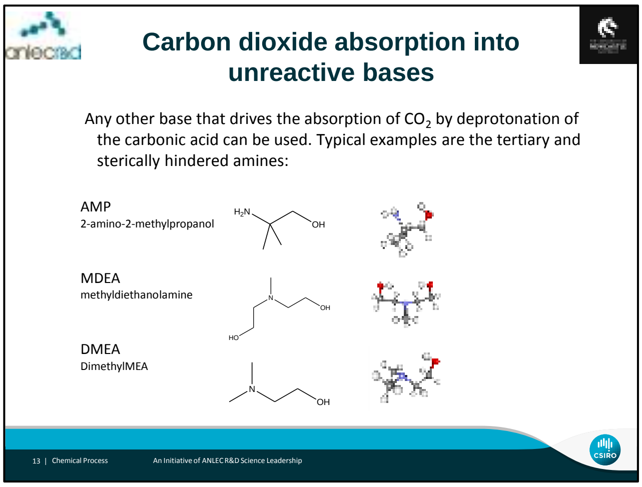
Reactions of CO_2 in basic aqueous solution

In this slide is an example of the insight that can be gained from modelling the relatively complex processes that CO_2 undergoes in basic solution.

The top panels represent the reaction of 30mM CO_2 in a 15mM CO_3^{2-} solution; the lower panels shows the processes with the replacement of 15mM CO_3^{2-} with 15mM OH^-. In both solutions 15 mM CO_2 is absorbed but the reaction is significantly faster for the OH^- solution.

The reaction is producing carbonic acid which immediately releases a proton and thus the pH drops during the reaction. This is shown in the right hand panels. For the CO_3^{2-} solution it takes about 2 sec for the final pH drop which indicates the exhaustion of the base; for the OH^- solution it takes only 1 sec.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into unreactive bases

Any other base that drives the absorption of CO_2 by deprotonation of the carbonic acid can be used. Typical examples are the tertiary and sterically hindered amines:

AMP
2-amino-2-methylpropanol

MDEA
methyldiethanolamine

DMEA
DimethylMEA

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Tertiary amines

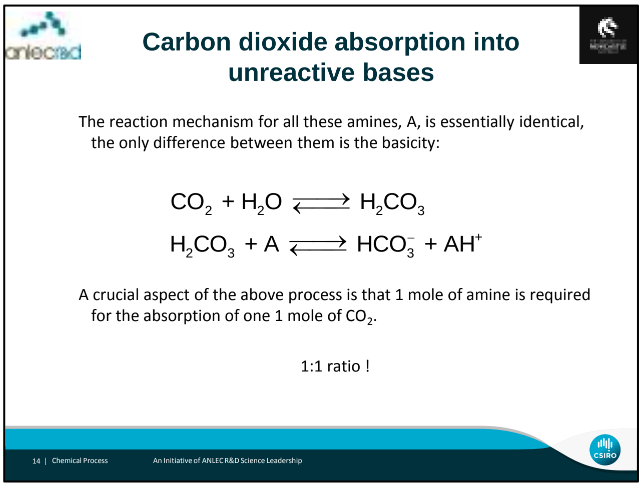
Instead of carbonate or hydroxide, any other base can potentially be used. Organic amines are the most prominent alternatives.

We have to distinguish between so-called reactive and unreactive bases. Reactivity refers to the formation of carbamates which will be discussed in a moment.

Most unreactive bases are tertiary amines as they cannot form the carbamate and their only relevant property is the basicity, the ability to react with a proton. The most prominent members for PCC are MDEA (methyldiethanolamine) and DMEA (dimethylMEA).

An alternative to tertiary amines sterically hindered secondary and primary amines such as AMP (2-amino-2-methylpropanol) also do not react directly with CO_2. While here carbamates could theoretically form, they do not as there is not enough space around the amine group for the incoming CO_2.

Reactions of CO_2 with H_2O and OH^-



Carbon dioxide absorption into unreactive bases

The reaction mechanism for all these amines, A, is essentially identical, the only difference between them is the basicity:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

$$H_2CO_3 + A \rightleftarrows HCO_3^- + AH^+$$

A crucial aspect of the above process is that 1 mole of amine is required for the absorption of one 1 mole of CO_2.

1:1 ratio !

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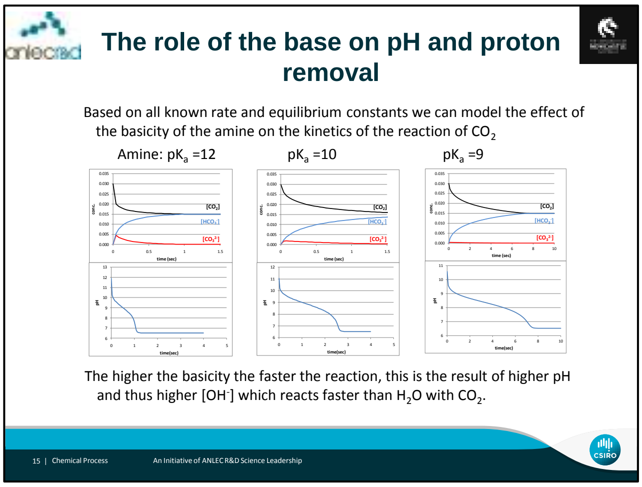
The role of the base

The only function of the non-reactive base A is to act as a Brønsted base and absorb a proton. The proton comes from a carbonic acid molecule which is contains a CO_2 molecule. In this way the reaction is pulled towards the products and as a result CO_2 is absorbed into the amine solution.

The only difference between such amines is the protonation constant or their basicities. They are often quantified as pK_a values.

An important aspect is that there is a net 1:1 interaction between a CO_2 and an amine molecule.

Reactions of CO_2 with H_2O and OH^-



The role of the base on pH and proton removal

Based on all known rate and equilibrium constants we can model the effect of the basicity of the amine on the kinetics of the reaction of CO_2

The higher the basicity the faster the reaction, this is the result of higher pH and thus higher $[OH^-]$ which reacts faster than H_2O with CO_2.

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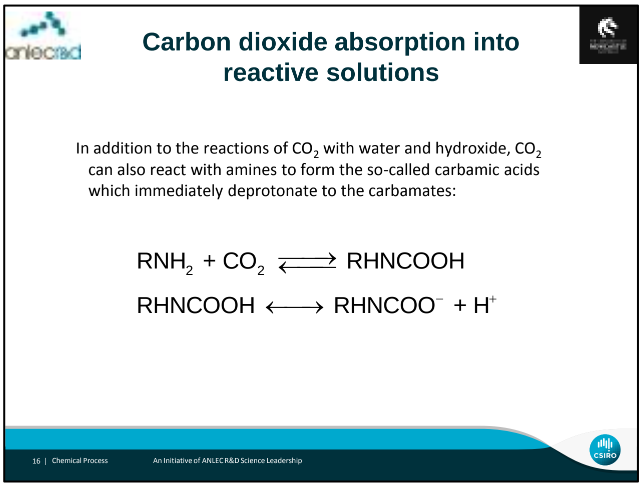
The effect of the basicity of the amine

Even if these non-reactive amines do not directly interact with CO_2, they indirectly influence the reaction via the pH of the solution. More basic amines with create a higher pH of the solution which increases the hydroxide concentration and this in turn accelerates the reaction of CO_2 to form the bicarbonate as the hydroxide ion reacts faster than water.

This is illustrated in the slide. It shows the concentration profiles of CO_2, HCO_3^- and CO_3^{2-} as a function of time for three fictional tertiary amines with pK_a values of 12, 10 and 9. The initial concentrations are $[A]_0$=0.015 M and $[CO_2]_0$=0.03 M; thus an excess of CO_2.

For the most basic amine it takes about 1 sec for the reaction to reach the final equilibrium, this is best indicated by the drop of pH; for the second amine it takes some 2.5 sec and for the third amine it takes more than 5 sec.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

In addition to the reactions of CO_2 with water and hydroxide, CO_2 can also react with amines to form the so-called carbamic acids which immediately deprotonate to the carbamates:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

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CO_2 reactions with amines to form carbamates

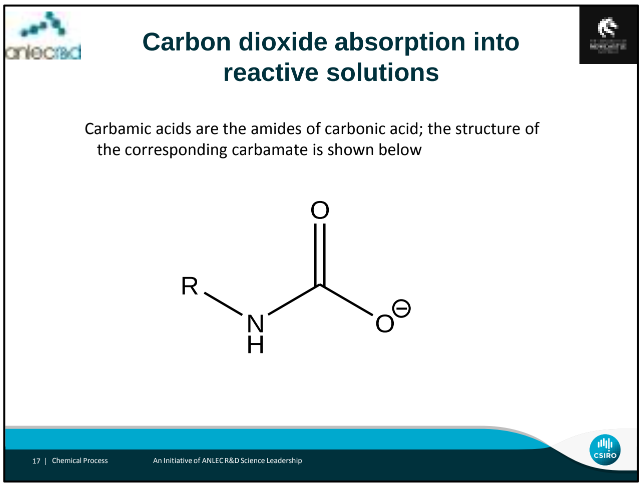
Parallel to the reactions of CO_2 with water and hydroxide to form carbonic acid and bicarbonate, CO_2 reacts with some amines to form the carbamic acid. This is a fast and reversible reaction defined by a forward and back rate constant:

Equation

The initially formed carbamic acid has a protonation constant of around logK=7, thus at pH values relevant for PCC which are around 9, the carbamic acid is deprotonated to form the much more stable carbamate.

equation

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

Carbamic acids are the amides of carbonic acid; the structure of the corresponding carbamate is shown below

17 | Chemical Process

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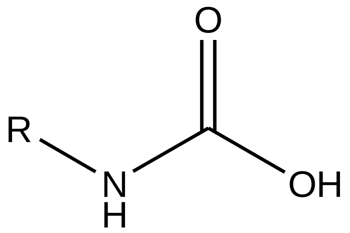
The carbamate

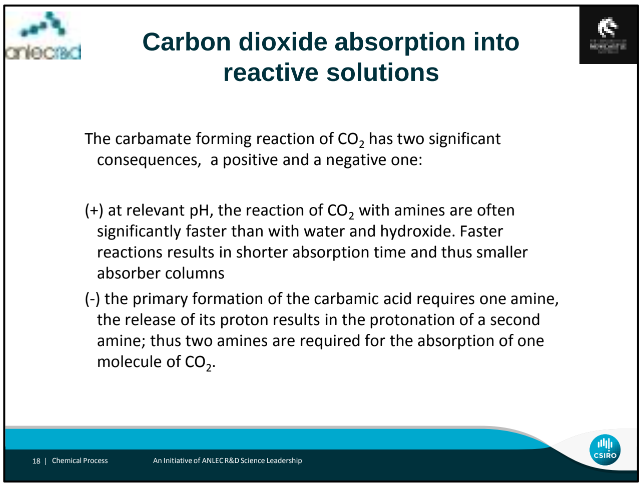
Carbamic acids are the mono-amides of carbonic acids. (The di-amides are called ureas, they are much more stable than the carbamic acids, they do not form under PCC conditions.)

The structure of carbamic acid is shown in the figure. Carbamic acid is often shown as a zwitter ion with the OH proton moved to the amine nitrogen. This is not correct, amides are very weak bases and are not protonated under normal circumstances.



The carbamate, deprotonated carbamic acid, features the carboxylate group with a negative charge (-COO^-). Under PCC conditions, pH, only the carbamate exists to any significant amount.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

(+) at relevant pH, the reaction of CO_2 with amines are often significantly faster than with water and hydroxide. Faster reactions results in shorter absorption time and thus smaller absorber columns

(-) the primary formation of the carbamic acid requires one amine, the release of its proton results in the protonation of a second amine; thus two amines are required for the absorption of one molecule of CO_2.

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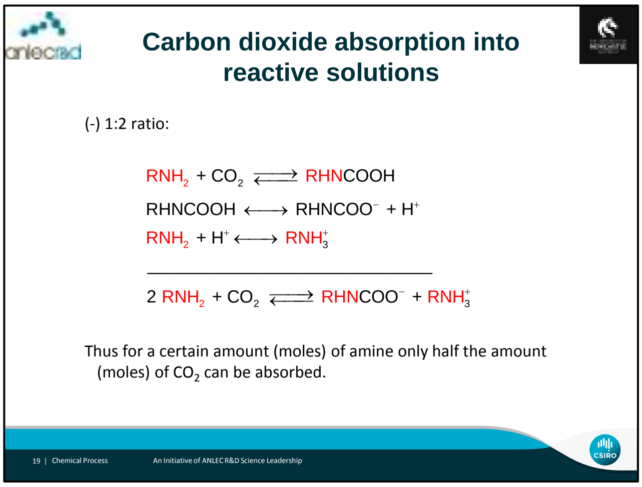
The relevance of the formation of the carbamate

The reaction of CO_2 with amines to form the carbamic acid is usually much faster than the reactions with water and hydroxide. This is a significant advantage as faster reactions results in faster absorption of CO_2 and eventually allows the usage of a shorter absorber column. The savings in capital expenditure is significant and steal is not getting cheaper. Thus the formation of carbamates is an **advantage**.

The **disadvantage** is the release of a proton by the carbamic acid; under PCC conditions it is picked up by an amine. Thus two amine molecules are required for each molecule of absorbed CO_2; one for the formation of the carbamic acid and one for the reaction with the released proton. Overall only half as much CO_2 can be absorbed compared with amines that do not form carbamates. For most amines both processes, carbamate formation and reaction of CO_2 with water/hydroxide occur simultaneously and the ratio never reaches 1:2.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

(-) 1:2 ratio:

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

$$2\ RNH_2 + CO_2 \rightleftarrows RHNCOO^- + RNH_3^+$$

Thus for a certain amount (moles) of amine only half the amount (moles) of CO_2 can be absorbed.

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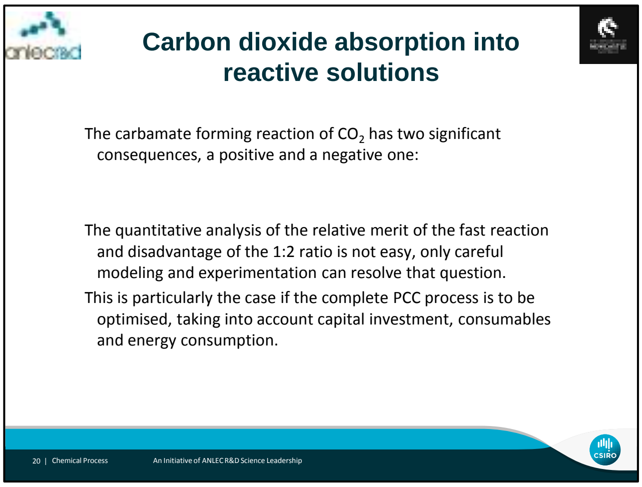
The chemical equations

The formation of the carbamates in aqueous solution under conditions relevant for PCC is a rather complex process which can be divided into the individual steps:

- The first step is the reaction of CO_2 with the amine to form carbamic acid
- The carbamic acid can undergo deprotonation, it is in equilibrium with the carbamate and a proton. The pH in PCC is usually high enough so the equilibrium is far on the carbamate side.
- The proton is picked up by an additional amine.
- The overall reaction is indicated under the line, it clearly shows the 1:2 ratio, per one CO_2 molecule two amine molecules are required.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

The quantitative analysis of the relative merit of the fast reaction and disadvantage of the 1:2 ratio is not easy, only careful modeling and experimentation can resolve that question.

This is particularly the case if the complete PCC process is to be optimised, taking into account capital investment, consumables and energy consumption.

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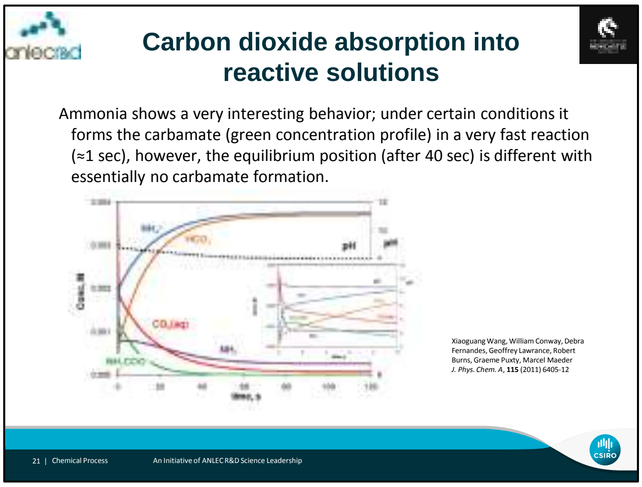
Summary advantages and disadvantages of carbamate formation

As carbamate formation has two opposite effects, it is not easy to assess the overall advantage for the PCC process. Faster reactions results in reduced size of the absorber, the unfavourable 1:2 ratio results in reduced CO_2 uptake per volume of amine solution.

Carful modelling of all facets of the process is crucial, this includes very different aspects such as capital investment in the construction of the plant, running costs in terms of consumables (most amines tend to decompose) and very importantly in terms of energy consumption which includes a variety of components such as the pumping of solutions and the heating of the CO_2 rich amine solution in the stripper.

Reactive amines that form carbamates



Carbon dioxide absorption into reactive solutions

Ammonia shows a very interesting behavior; under certain conditions it forms the carbamate (green concentration profile) in a very fast reaction (≈1 sec), however, the equilibrium position (after 40 sec) is different with essentially no carbamate formation.

Xiaoguang Wang, William Conway, Debra Fernandes, Geoffrey Lawrance, Robert Burns, Graeme Puxty, Marcel Maeder
J. Phys. Chem. A, **115** (2011) 6405-12

21 | Chemical Process An Initiative of ANLEC R&D Science Leadership

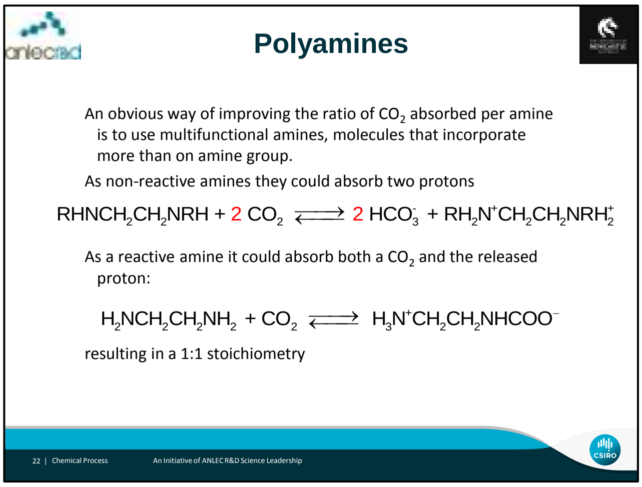
Ammonia forms a transient carbamate

Ammonia is featuring a surprising behaviour with respect to carbamate formation.

As we have seen carbamate formation is advantageous from the kinetic point of view but disadvantageous because of the unfavourable 1:2 ratio. Under certain conditions ammonia reacts to form carbamate without the disadvantage. Consider the concentration profiles in the slide, they represent the concentration changes during the reaction of 3.8 mM CO_2 in 4.0 mM ammonia: within about 1 sec some 40% of the total CO_2 reacts to form the carbamate. This reaction results in a pH-drop from about 10 to 9. Under such conditions the carbamate is less stable and slowly decomposes almost completely within 1 min.

While the conditions for the above calculations are not relevant for PCC, this example demonstrates that carful modelling of complex reactions can result in the detection and identification of interesting behaviours.

Reactive amines that form carbamates



Polyamines

An obvious way of improving the ratio of CO_2 absorbed per amine is to use multifunctional amines, molecules that incorporate more than on amine group.

As non-reactive amines they could absorb two protons

$$RHNCH_2CH_2NRH + 2\ CO_2 \rightleftharpoons 2\ HCO_3^- + RH_2N^+CH_2CH_2NRH_2^+$$

As a reactive amine it could absorb both a CO_2 and the released proton:

$$H_2NCH_2CH_2NH_2 + CO_2 \rightleftharpoons H_3N^+CH_2CH_2NHCOO^-$$

resulting in a 1:1 stoichiometry

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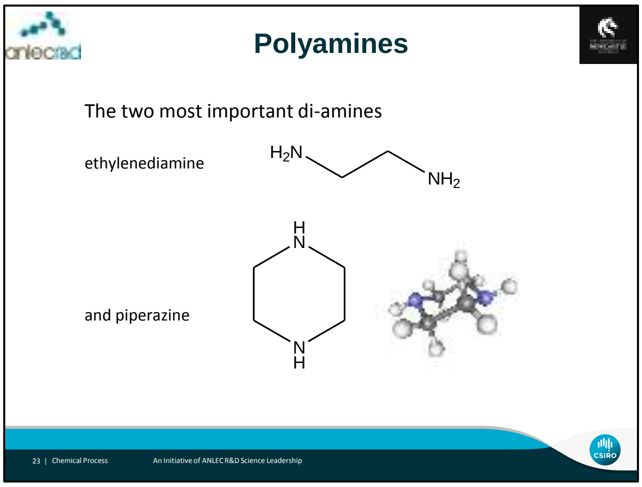
Di-amines to improve the CO_2:amine ratio

Under relevant conditions two amines are required to absorb one molecule of CO_2. One amine to form the carbamate the other to absorb a proton that is released in the carbamate formation.

An obvious way dealing with that problem is to use di-amines, compounds that contain two amine groups. One amine group is forming the carbamate while the other is absorbing the proton; this results in a desirable 1:1 stoichiometry.

On paper this looks great, however there are many additional aspects that need to be taken into account: solubility, stability, price, etc. No doubt more diamines are promising and their investigation is being pursued in many laboratories.

Reactive amines that form carbamates



Polyamines

The two most important di-amines

ethylenediamine

and piperazine

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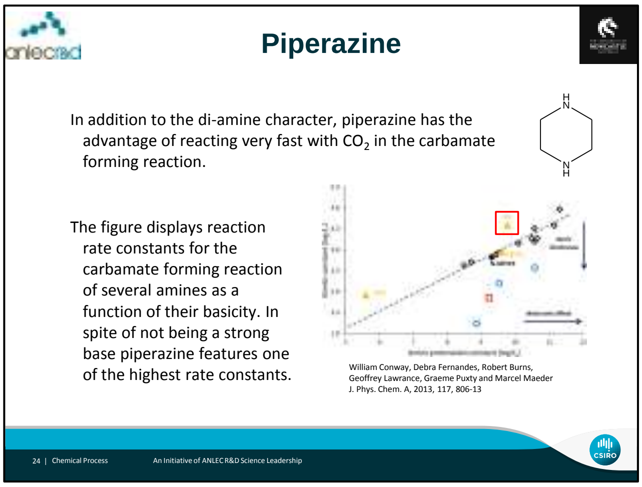
Ethylene-diamine and piperazine

The most prominent diamines are ethylene-diamine and piperazine. Ethylene-diamine is a relative of MEA, a linear molecule with primary amine groups at both ends.

A very well investigated molecule is piperazine. It is a six-membered ring with two secondary amines in trans position. The carbamate forming reaction is very fast and thus the molecule is promising. Detailed investigation of the complete reaction mechanism is much more difficult as the di-carbamate also forms. The existence of several protonation equilibria at the carbamate groups make life even more difficult.

There is little doubt that piperazine will be tested much more.

Reactive amines that form carbamates



Piperazine

In addition to the di-amine character, piperazine has the advantage of reacting very fast with CO_2 in the carbamate forming reaction.

The figure displays reaction rate constants for the carbamate forming reaction of several amines as a function of their basicity. In spite of not being a strong base piperazine features one of the highest rate constants.

William Conway, Debra Fernandes, Robert Burns, Geoffrey Lawrance, Graeme Puxty and Marcel Maeder
J. Phys. Chem. A, 2013, 117, 806-13

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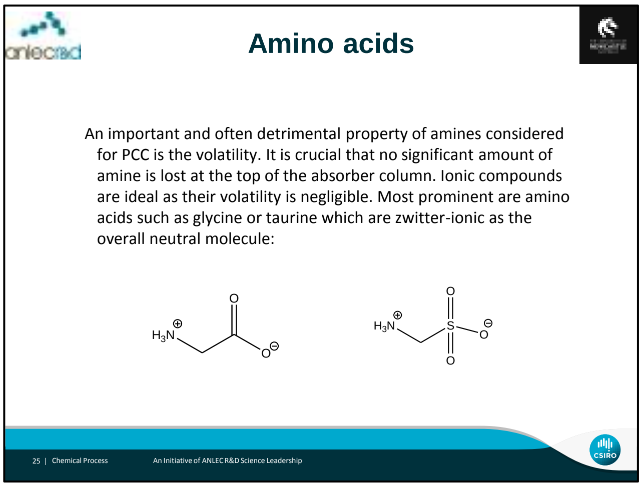
Piperazine

Piperazine is an interesting diamine for several reasons; most prominent is its surprisingly fast reaction with CO_2 to form the carbamate.

The graph in the powerpoint slide is a plot that attempts at relating the rate constant for carbamate formation to the basicity of several amines. For most investigated amines there is a rather straightforward linear relationship indicated by the dotted line. Several amines are under the line and most of these observations can be understood as steric effects, the CO_2 molecule is much larger than the proton and thus needs more free space around the amine nitrogen, if it is not available the rate is slower.

Piperazine is above the line and thus reacts faster than expected. Presently no reason can be given for this interesting observation.

Reactive amines that form carbamates



Amino acids

An important and often detrimental property of amines considered for PCC is the volatility. It is crucial that no significant amount of amine is lost at the top of the absorber column. Ionic compounds are ideal as their volatility is negligible. Most prominent are amino acids such as glycine or taurine which are zwitter-ionic as the overall neutral molecule:

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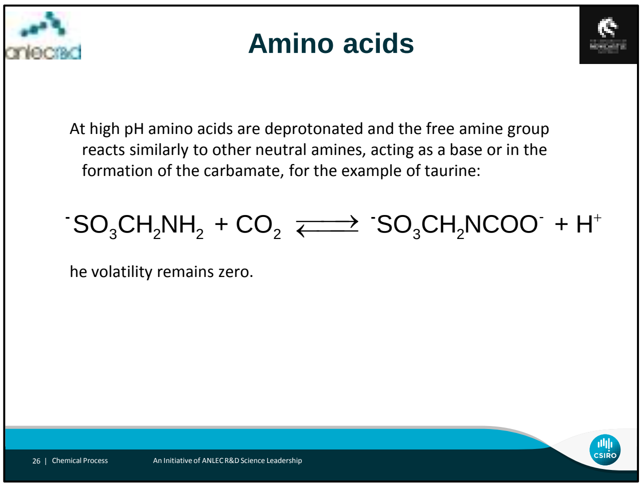
Non-volatile amino acids

A major problem with most amines is their volatility. The stripper operates at elevated temperatures (around 120-140°C) and at these temperatures most amines have a substantial vapour pressure, they will evaporate and need to be separated from the CO_2. Ammonia, of course, is the worst of them all.

Amino-acids feature the distinctive property of being charged at all pH values: at high pH the amine and the carboxylate are deprotonated and thus the charge is -1; at low pH both groups are protonated and the charge is +1. At intermediate pH values the proton is attached to the amine and not the carboxylate group and thus the molecule is a zwitter ion. While overall it is neutral, the zwitter-ion character results in a very low volatility.

As expected several research groups investigate amino acids for their PCC potential.

Reactive amines that form carbamates



Amino acids

At high pH amino acids are deprotonated and the free amine group reacts similarly to other neutral amines, acting as a base or in the formation of the carbamate, for the example of taurine:

$$^{-}SO_3CH_2NH_2 + CO_2 \rightleftharpoons {}^{-}SO_3CH_2NCOO^{-} + H^{+}$$

he volatility remains zero.

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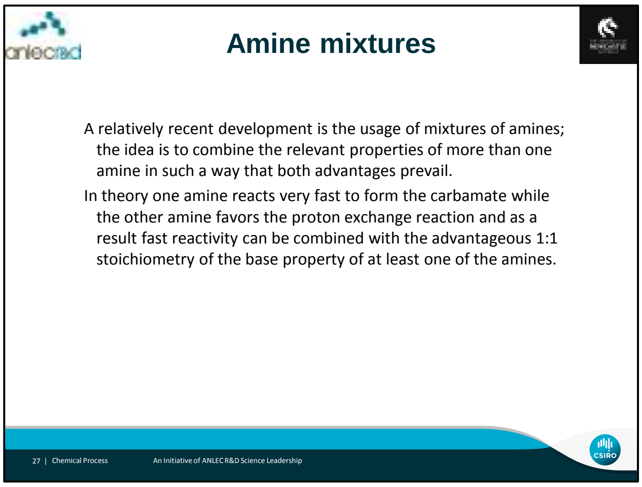
Taurine

Taurine is an unusual amino acid as the acid group is a sulfonic rather than a carboxylic acid; but taurine is still a naturally occurring amino acid with similar properties as the usual ones, in particular the property of being charged at any pH and thus being non-volatile. One interesting property is its relatively low second protonation constant of about 9.



Amine mixtures

A relatively recent development is the usage of mixtures of amines; the idea is to combine the relevant properties of more than one amine in such a way that both advantages prevail.

In theory one amine reacts very fast to form the carbamate while the other amine favors the proton exchange reaction and as a result fast reactivity can be combined with the advantageous 1:1 stoichiometry of the base property of at least one of the amines.

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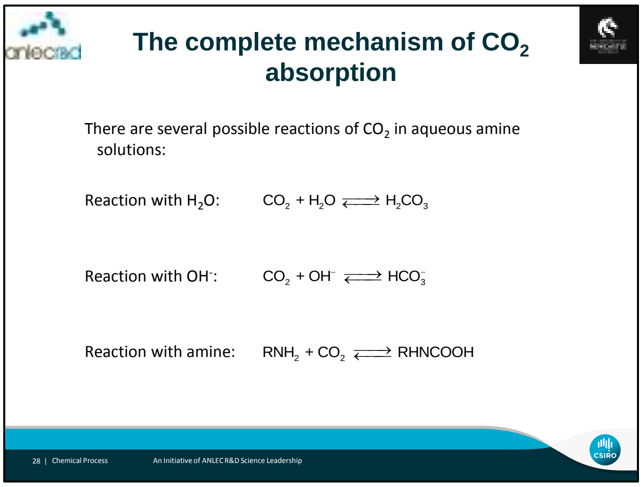
Mixtures of amines

The perfect amine encompasses so many properties that it is unlikely that it amine actually exists. An obvious option towards that goal is to combine different properties in on molecule which will have different substituents, each one with a preferable property; the diamines discussed earlier are just one example. The resulting molecule will be large, expensive and most likely not sufficiently soluble.

Probably a more promising and realistic approach is the employ a mixture of different molecules in the absorbing solutions, each one with a particularly useful property. An approach that is pursued by many research groups. Presently the best investigated idea is the combine a non-reactive amine that absorbs in a 1:1 ratio, with a fast, reactive amine such as piperazine.

As there is an infinity of such mixtures and mixture ratios it will not be possible to investigate their properties experimentally, either in the laboratory or the pilot plant. Well founded computational approaches are clearly preferable.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

There are several possible reactions of CO_2 in aqueous amine solutions:

Reaction with H_2O: $CO_2 + H_2O \rightleftarrows H_2CO_3$

Reaction with OH^-: $CO_2 + OH^- \rightleftarrows HCO_3^-$

Reaction with amine: $RNH_2 + CO_2 \rightleftarrows RHNCOOH$

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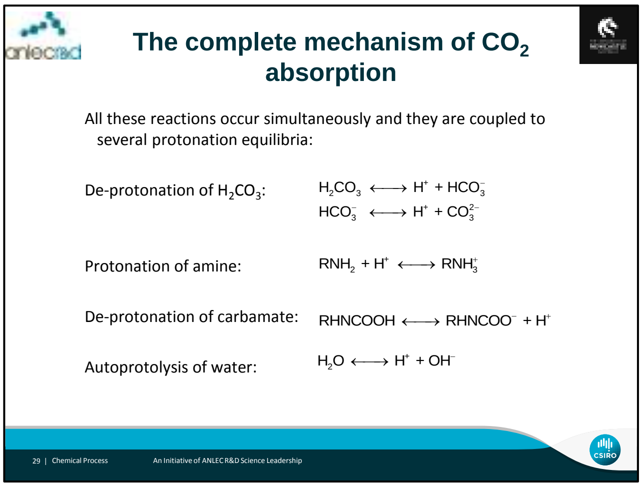
Amines that form carbamates

Most amines form the respective carbamate. As we have seen this reaction has positive and negative effects on the relevant properties of PCC.

One clear effect is that the additional reactions will add to the complexity of the chemistry of the process of CO_2 uptake in PCC. CO_2 has now three different reaction partners, all three reactions resulting in the uptake of dissolved CO_2. All three processes will occur parallel and it is the relative concentrations of the reaction partners that define the overall rate: the concentration of water is approximately constant and thus this path is fixed (pseudo-first order reaction); the hydroxy path is of course strongly pH dependent and the carbamate formation is dependent on the amine concentration. In addition the amine concentration will also influence the pH and thus the actual quantitative understanding requires substantial and detailed knowledge of all reactions involved.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

All these reactions occur simultaneously and they are coupled to several protonation equilibria:

De-protonation of H_2CO_3: $H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$

$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$

Protonation of amine: $RNH_2 + H^+ \longleftrightarrow RNH_3^+$

De-protonation of carbamate: $RHNCOOH \longleftrightarrow RHNCOO^- + H^+$

Autoprotolysis of water: $H_2O \longleftrightarrow H^+ + OH^-$

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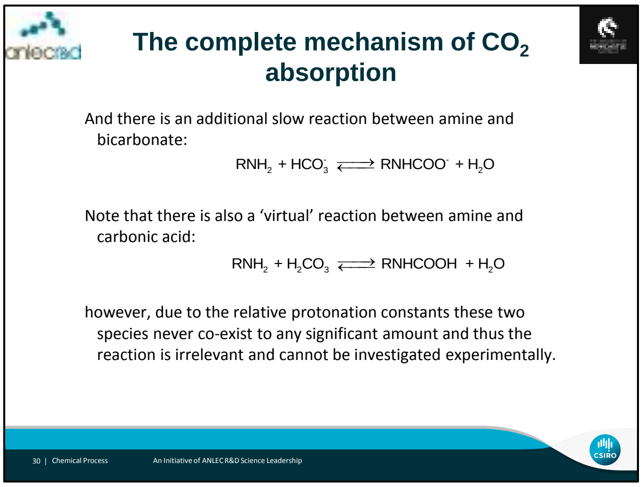
Carbamate formation and pH

There are several protonation equilibria that all play and change during the reaction of CO_2 in amine solutions.

The protonation equilibria of carbonate and bicarbonate, of the amine and the autoprotolysis of water are always active, also with non-carbamate forming amines. The carbamate adds another protonation equilibrium. The initial product of the reaction of CO_2 with the amine is the carbamic acid, however, under PCC conditions the acid is immediately deprotonated. The pK_a values of most known carbamates are between 7 and 8, substantially lower than the pH of a typical PCC solution, thus the carbamic acid exists only in very small concentrations.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

And there is an additional slow reaction between amine and bicarbonate:

$$RNH_2 + HCO_3^- \rightleftharpoons RNHCOO^- + H_2O$$

Note that there is also a 'virtual' reaction between amine and carbonic acid:

$$RNH_2 + H_2CO_3 \rightleftharpoons RNHCOOH + H_2O$$

however, due to the relative protonation constants these two species never co-exist to any significant amount and thus the reaction is irrelevant and cannot be investigated experimentally.

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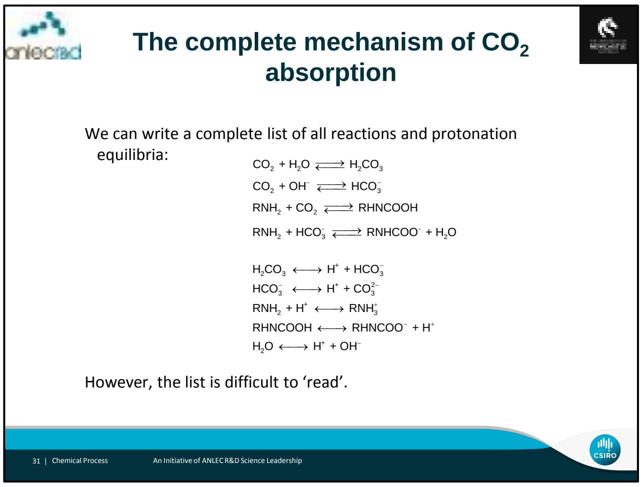
Carbamate formation with bicarbonate

Carbamate formation relevant for PCC is via the path just described, CO_2 reacting reversibly with the amine to form initially carbamic acid which is immediately deprotonated.

Amines react also reversibly with the bicarbonate ion, HCO_3^-, in a much slower reaction to form the carbamate directly.

While this reaction is not relevant for carbamate formation it is important for its decomposition. If the only path for carbamate decomposition is via the carbamic acid, the carbamate would be increasingly more stable at increasing pH, essentially without a limit. The bicarbonate path provides the direct decomposition of the carbamate. The rate for that reaction is much slower than for the carbamic acid.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

We can write a complete list of all reactions and protonation equilibria:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$CO_2 + OH^- \rightleftarrows HCO_3^-$$
$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$
$$RNH_2 + HCO_3^- \rightleftarrows RNHCOO^- + H_2O$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$
$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$
$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$
$$H_2O \longleftrightarrow H^+ + OH^-$$

However, the list is difficult to 'read'.

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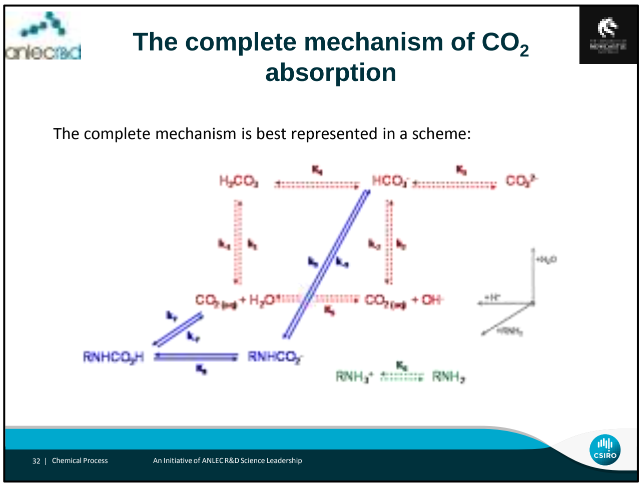
The complete reaction scheme for reactive amines

It is straightforward to collect all the individual reactions that can occur in aqueous amine solutions in the presence of dissolved CO_2.

There are four reversible reactions and five instantaneous protonation equilibria. The protonation equilibria are quantitatively described by five equilibrium constants; four of them are known the amine protonation constant if unknown can be determined easily, the only unknown equilibrium constant it the carbamate protonation constant. Two of the reversible reactions are also known, the remaining two reversible carbamate formation reactions need to be determined for each amine. Altogether after the determination of the four rate constants plus the one protonation constant, any amine is completely defined. This of course only at the particular temperature, if all temperature dependences are known, everything is known and the reactions can be completely modelled under all conditions, at least as long as activity coefficients are be estimated to a reasonable level.

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

The complete mechanism is best represented in a scheme:

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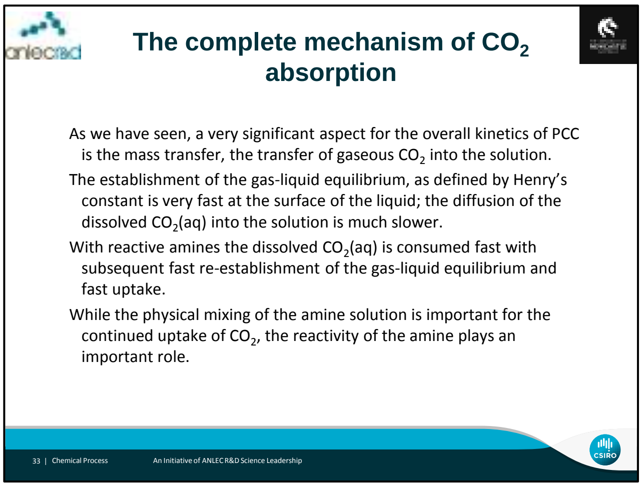
The complete reaction mechanism, graphically

It is possible to represent the complete reaction mechanism graphically. This is attempted in the slide above:

- In red we have the interactions of CO_2 in aqueous solution in the absence of amines
- In green the protonation equilibrium of the amine
- In blue the reactions relevant for carbamate formation and dissociation
- The pH is indicated in the right-left direction with high pH to the right
- The reactions with water/hydroxide are indicated in the up-down direction
- In the forward/backward direction we have the reactions of the CO_3/carbonate group with the amine

Reactive amines that form carbamates



The complete mechanism of CO_2 absorption

As we have seen, a very significant aspect for the overall kinetics of PCC is the mass transfer, the transfer of gaseous CO_2 into the solution.

The establishment of the gas-liquid equilibrium, as defined by Henry's constant is very fast at the surface of the liquid; the diffusion of the dissolved $CO_2(aq)$ into the solution is much slower.

With reactive amines the dissolved $CO_2(aq)$ is consumed fast with subsequent fast re-establishment of the gas-liquid equilibrium and fast uptake.

While the physical mixing of the amine solution is important for the continued uptake of CO_2, the reactivity of the amine plays an important role.

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Inclusion of mass transfer

The reactions of CO2 in aqueous amine solution are complex but manageable. It is important not to forget that the first step in the process is the transfer of the gaseous CO_2 into the amine solution. This mass transfer only occurs at the surface of the liquid and is largely independent of the liquid phase. However, as soon as the CO_2 is dissolved it will start the diffusion into the liquid phase and on the way it will undergo all the reactions that are available. This complete process is supported by the constant physical mixing of the solution as it travels down the absorber column. Of course the reverse is happening in the stripper column where a certain amount of the absorbed CO_2 is released back into the gas phase.

The computation of the chemical processes coupled to diffusion and physical mixing is exceedingly complex and has been tackled only recently