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

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

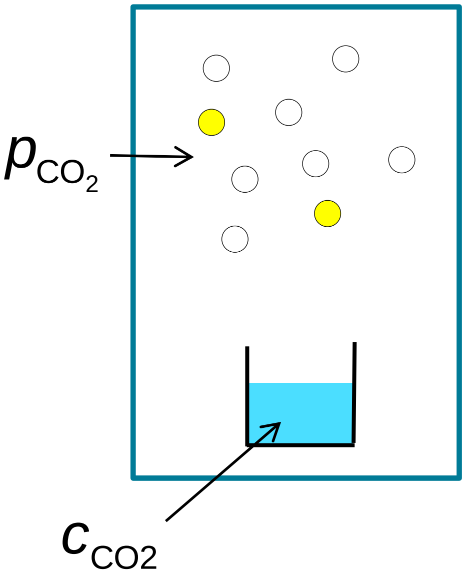
  - equilibrium
    - Henry's law

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."

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

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



Henry's Law

It is important to use the correct version/units for the equation !

A few examples:

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

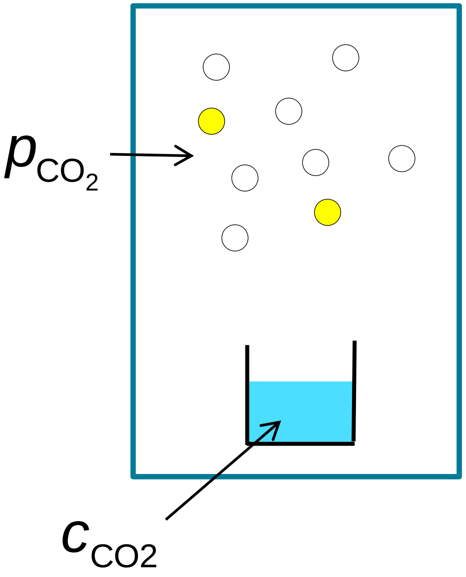
$$k_{h,px} = \frac{p}{x} = 0.163 \times 10^{4}\ \text{atm}$$

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

p = partial pressure, in atm

c = concentration, in mol/L

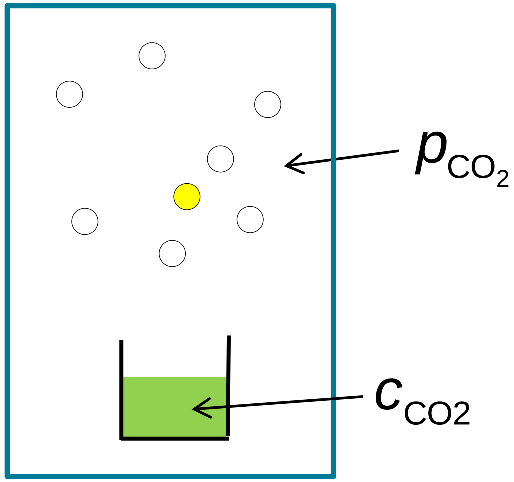
x = mole fraction, dimensionless



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.



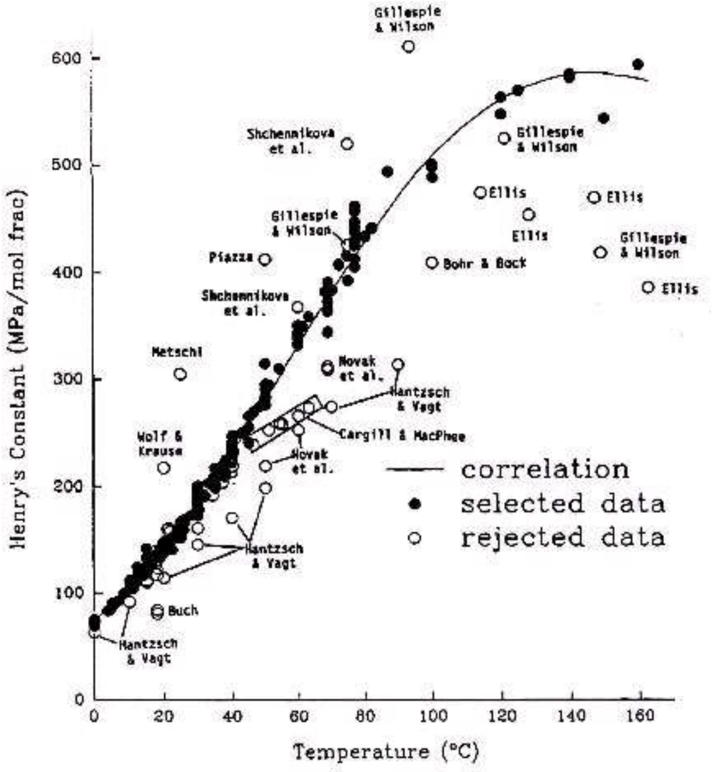
CO_2, N_2

NaOH, Na_2CO_3

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

Carbon dioxide absorption into water

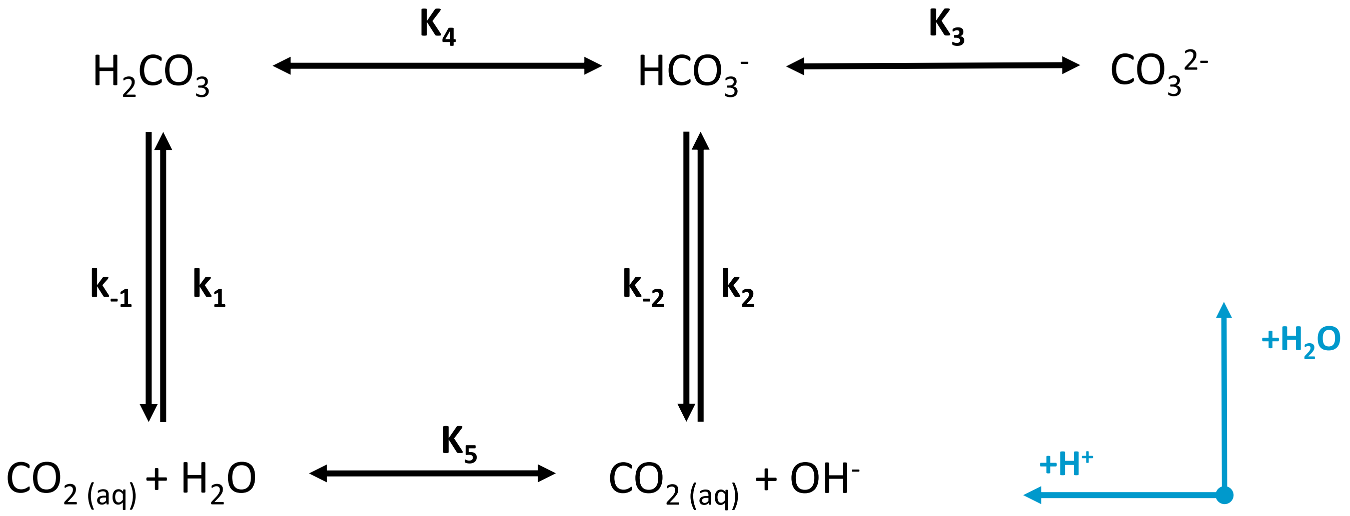
Once CO_2 is dissolved in water, several reactions occur simultaneously:

- Reaction of CO_2 with water and $$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
- Reaction with hydroxide $$CO_2 + OH^- \rightleftharpoons HCO_3^-$$
- 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 $\rightleftharpoons$ for slow reversible reactions and $\longleftrightarrow$ for fast (instantaneous) equilibria.

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:



K_4

K_3

H_2CO_3

HCO_3^-

CO_3^{2-}

k_{-1}

k_1

k_{-2}

k_2

$+H_2O$

$+H^+$

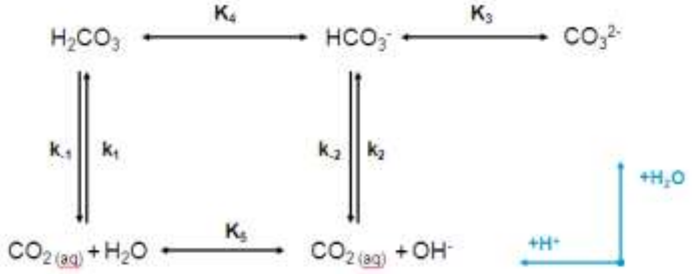
K_5

$CO_{2\,(aq)} + H_2O$

$CO_{2\,(aq)} + OH^-$

Reactions of carbon dioxide absorption in water

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



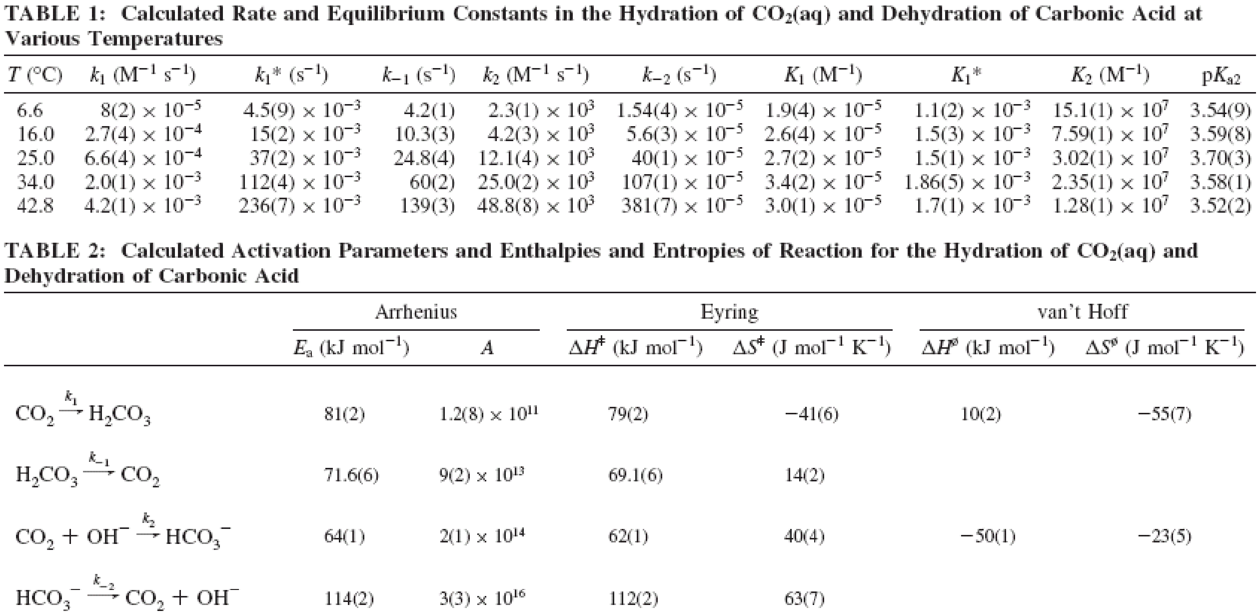


TABLE 1: Calculated Rate and Equilibrium Constants in the Hydration of CO_2(aq) and Dehydration of Carbonic Acid at Various Temperatures

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	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (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)		

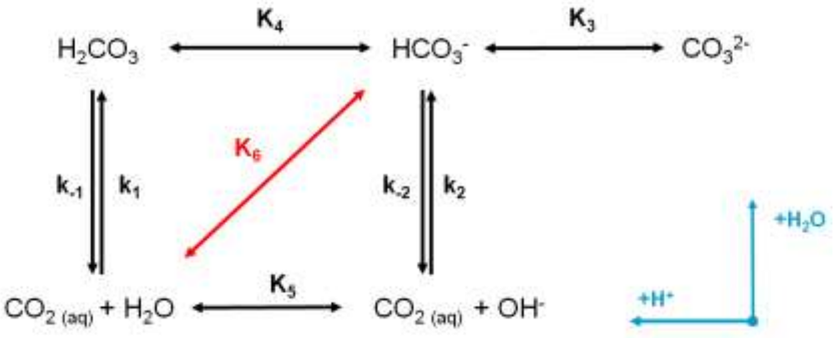
Xiaoguang Wang, William Conway, Robert Burns, Nichola McCann, and Marcel Maeder
J. *Phys. Chem. A* (2010) **114**, 1734–1740

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

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

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



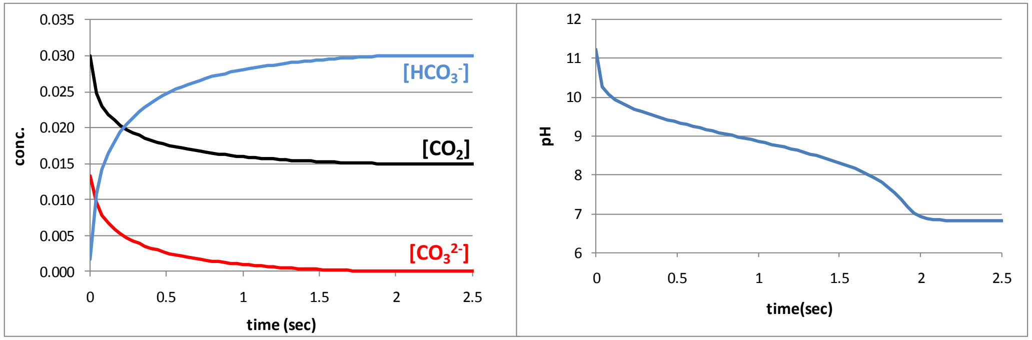
Reactions of carbon dioxide absorption in water

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.

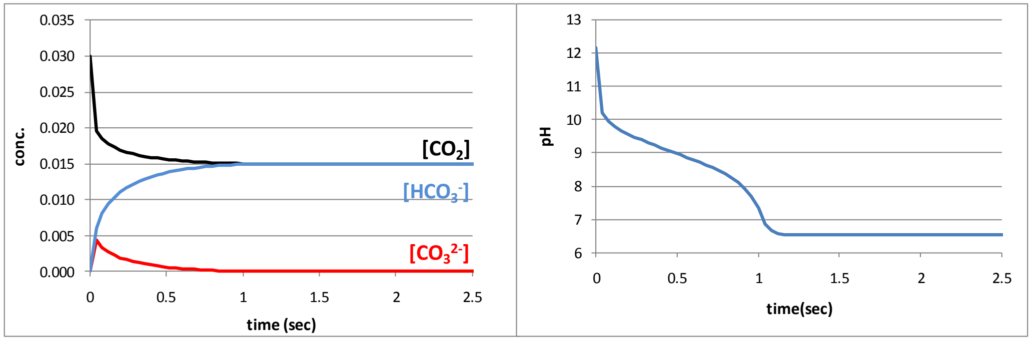
Reactions of carbon dioxide absorption in water

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^-

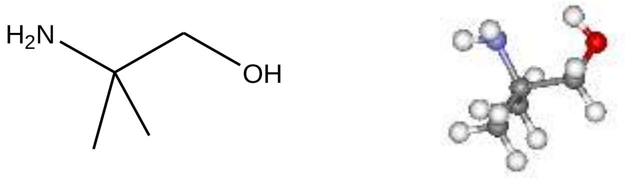


For the given concentrations the reaction with hydroxide is approximately twice as fast.

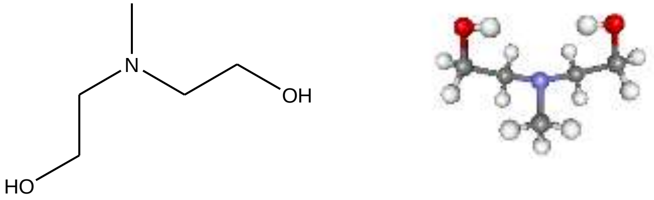
Carbon dioxide absorption into unreactive bases

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:

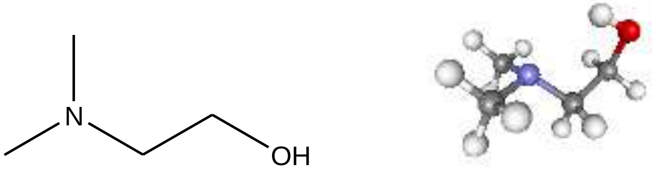
AMP
2-amino-2-methylpropanol



MDEA
methyldiethanolamine



DMEA
DimethylMEA



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:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

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

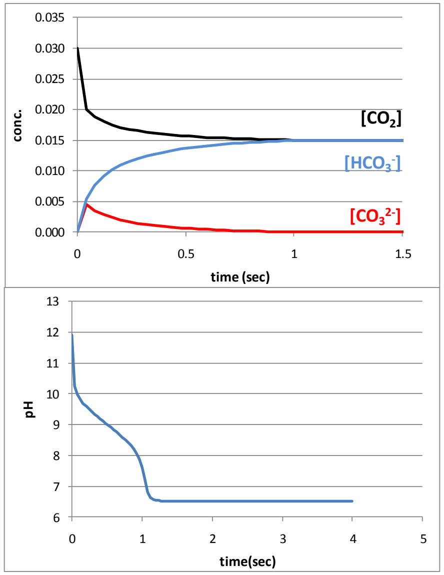
A crucial aspect of the above process is that 1 mole of amine is required for the absorption of one 1 mole of CO_2.

1:1 ratio !

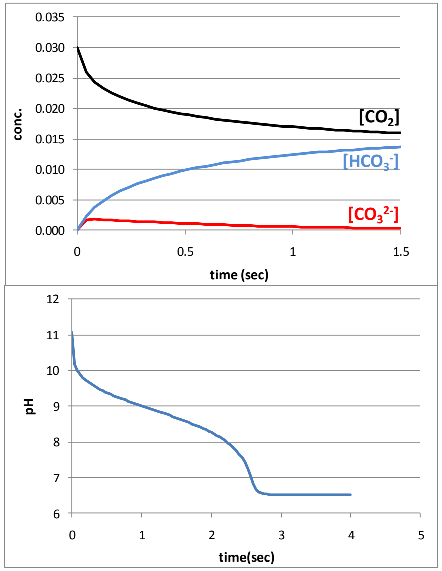
The role of the base on pH and proton removal

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

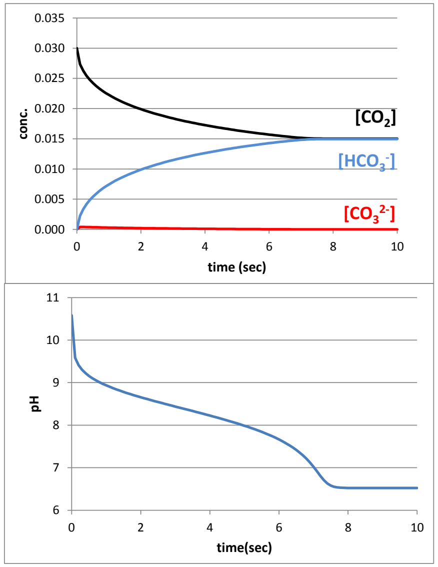
Amine: $pK_a = 12$



$pK_a = 10$



$pK_a = 9$



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.

Carbon dioxide absorption into reactive solutions

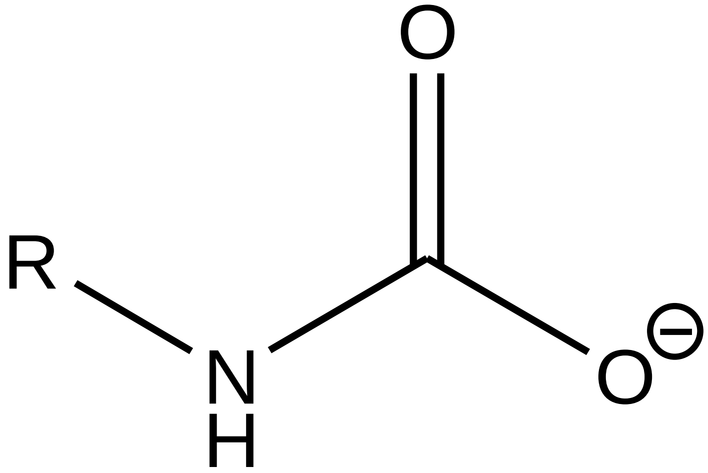
In addition to the reactions of CO_2 with water and hydroxide, CO_2 can also react with amines to form the so-called carbamic acids which immediately deprotonate to the carbamates:

$$RNH_2 + CO_2 \rightleftharpoons RHNCOOH$$

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

Carbon dioxide absorption into reactive solutions

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



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.

Carbon dioxide absorption into reactive solutions

(-) 1:2 ratio:

$$RNH_2 + CO_2 \rightleftharpoons RHNCOOH$$

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

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

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

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

Carbon dioxide absorption into reactive solutions

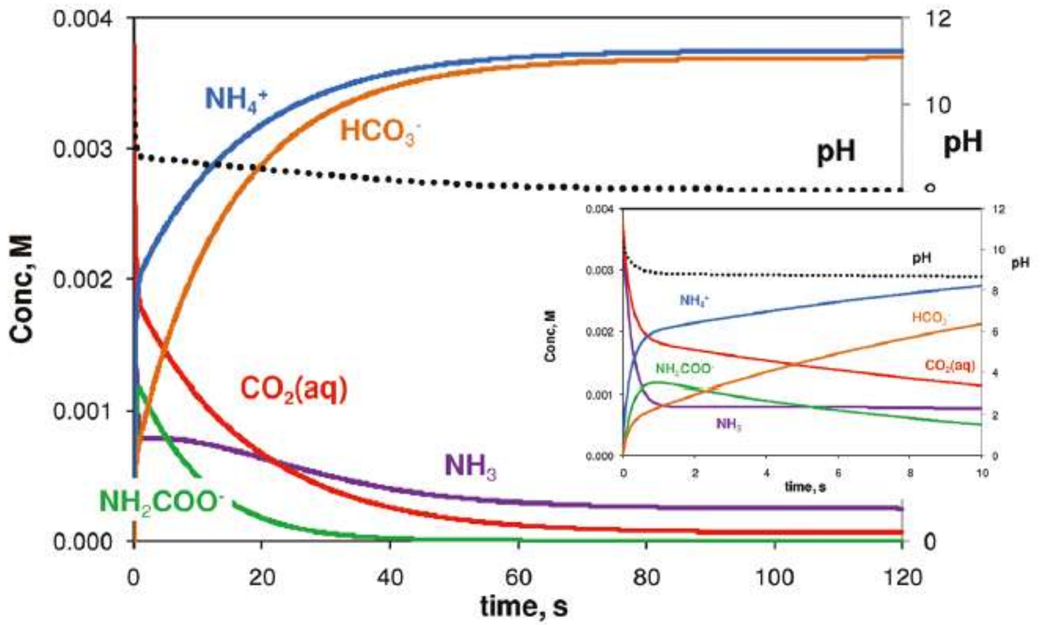
The carbamate forming reaction of CO_2 has two significant consequences, a positive and a negative one:

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.

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

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:

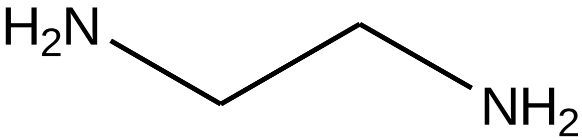
$$H_2NCH_2CH_2NH_2 + CO_2 \rightleftharpoons H_3N^+CH_2CH_2NHCOO^-$$

resulting in a 1:1 stoichiometry

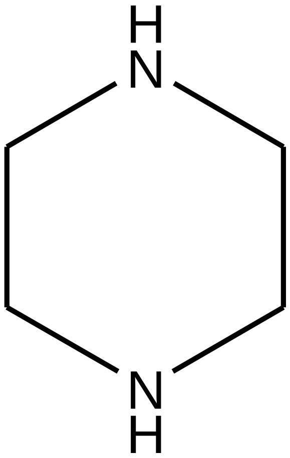
Polyamines

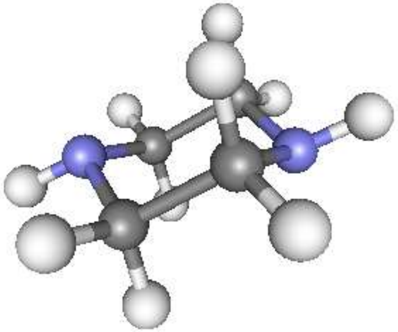
The two most important di-amines

ethylenediamine

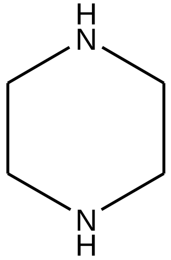


and piperazine



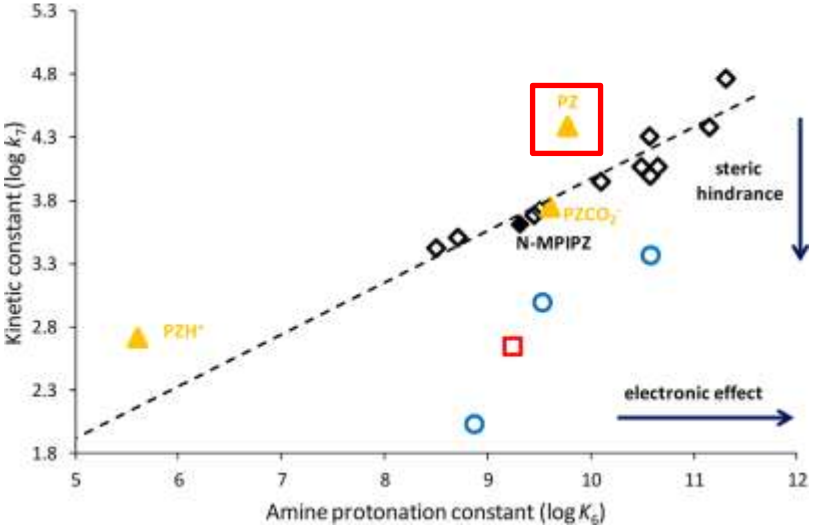


Piperazine



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

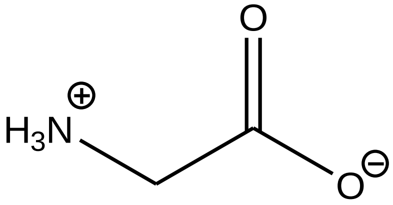
The figure displays reaction rate constants for the carbamate forming reaction of several amines as a function of their basicity. In spite of not being a strong base piperazine features one of the highest rate constants.

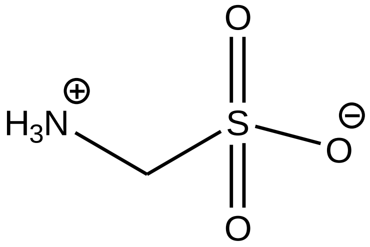


William Conway, Debra Fernandes, Robert Burns, Geoffrey Lawrance, Graeme Puxty and Marcel Maeder J. Phys. Chem. A, 2013, 117, 806-13

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:





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:

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

The volatility remains zero.

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.

The complete mechanism of CO_2 absorption

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

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

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

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

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:

$$H_2O \longleftrightarrow H^+ + OH^-$$

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.

The complete mechanism of CO_2 absorption

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

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

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

$$RNH_2 + CO_2 \rightleftarrows RHNCOOH$$

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

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

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

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

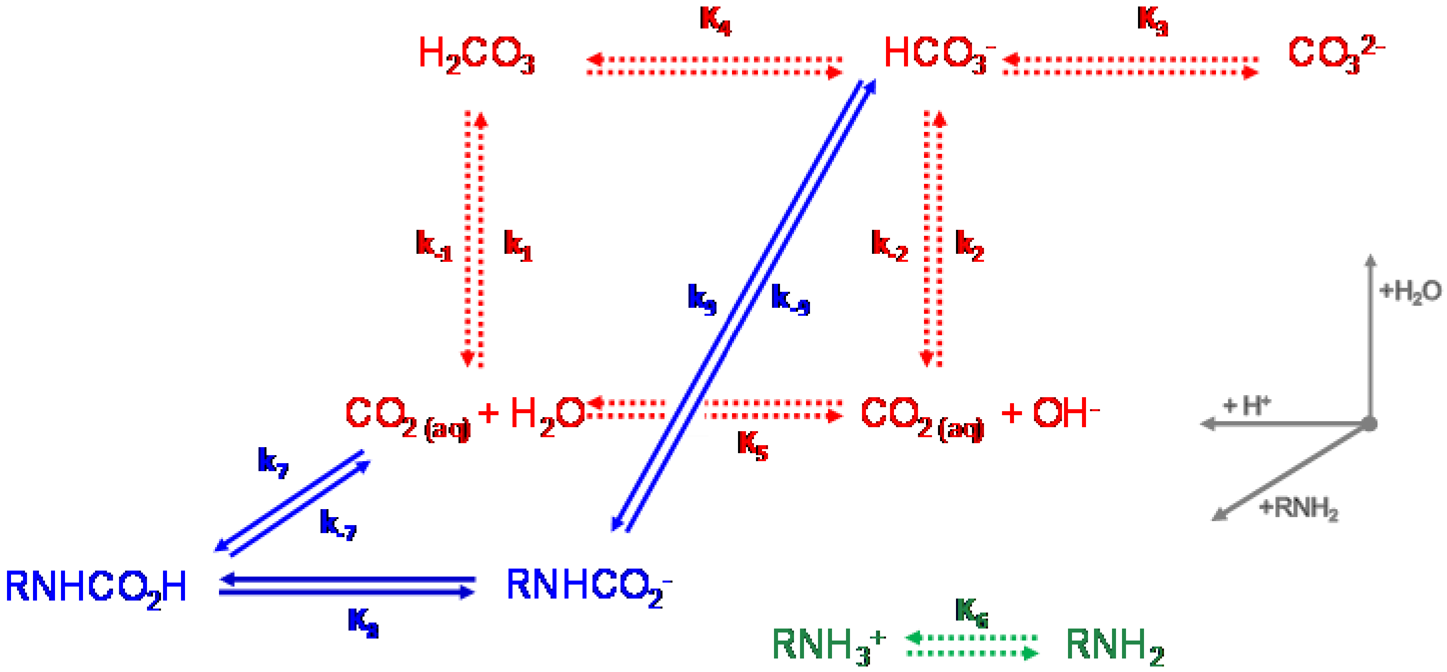
$$RHNCOOH \longleftrightarrow RHNCOO^- + H^+$$

$$H_2O \longleftrightarrow H^+ + OH^-$$

However, the list is difficult to ‘read’.

The complete mechanism of CO_2 absorption

The complete mechanism is best represented in a scheme:



H_2CO_3 $\xleftrightarrow{K_4}$ HCO_3^- $\xleftrightarrow{K_3}$ CO_3^{2-}

k_{-1} k_1

k_{-2} k_2

k_9 k_{-9}

$CO_{2\,(aq)} + H_2O$ $\xleftrightarrow{K_5}$ $CO_{2\,(aq)} + OH^-$

k_7 k_{-7}

$RNHCO_2H$ $\xleftrightarrow{K_8}$ $RNHCO_2^-$

RNH_3^+ $\xleftrightarrow{K_6}$ RNH_2

$+H_2O$

$+H^+$

$+RNH_2$

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.