

Advances in Hard-Modelling of Chemical Processes

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What is Chemometrics?

**The art of extracting
information from
measurements**

What are the options?

Soft	Firm (Statistical)	Hard
EFA, ALS etc	Classification /PLS type	Model fitting
Based on restrictions	Based on calibration set	Based on chemical model
Resolution of chromatogram	Octane rating of petrol	Reaction $A \rightarrow B \rightarrow C$

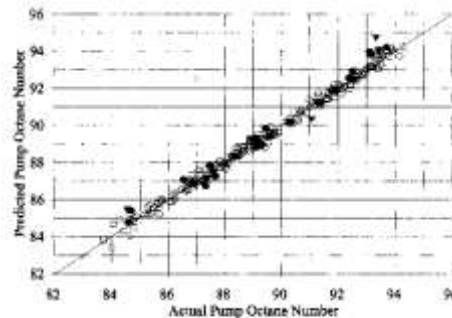
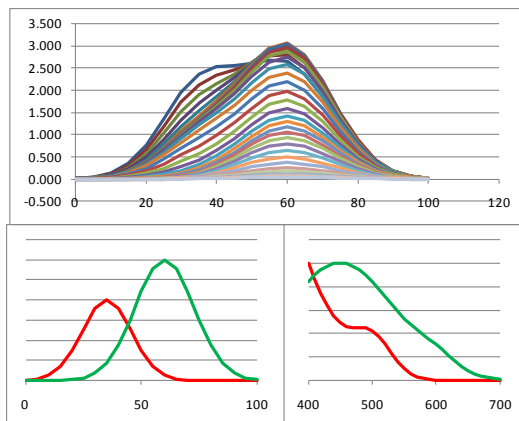
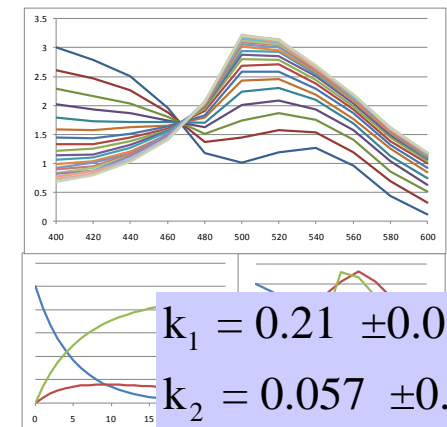


Figure 5. Predicted versus actual plot for pump octane number: ● (total of 175), samples which were included in the training set; ● (total of 20), samples in the test set; and ▼ (total of 8), highly leveraged samples which were removed from the training set prior to constructing the PLS regression model.



What are the options?

Soft	Firm (Statistical)	Hard
EFA, ALS etc	PCR/PLS type	Model fitting

Literature (Chemometrics)

intermediate	large	very small
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Why hard-modelling, why not soft-modelling?

M F Delaney, Analytical Chemistry, 1984, 56, 261R - 277R

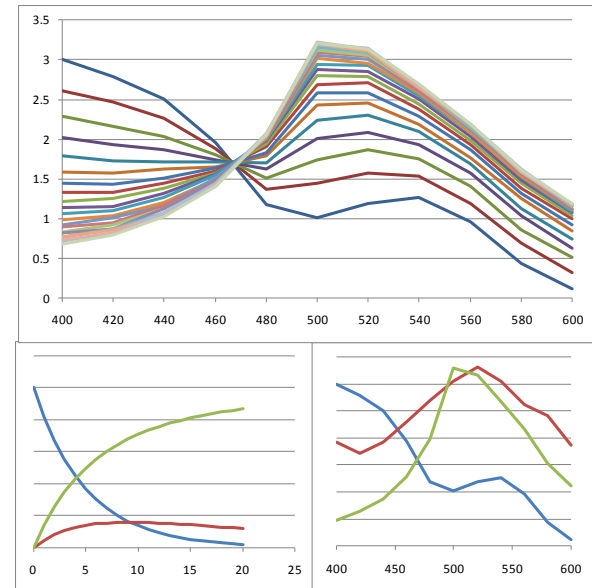
“ The methods can be classified into two groups - those in which assumptions about the system are made (e.g., number or identity of components, line shapes) and those in which no assumptions are made, other than (perhaps) linear system behavior. **In the former case you get back what you assumed, in the latter you get what you get. “**

Advantages of Hard-Modelling

Analysis generally much more robust than model-free analyses

Numerical values for essential constants, they can be

- tabled
- compared with other values
- interpreted
- analysed
- etc.



$$k_1 = 0.21 \pm 0.02$$

$$k_2 = 0.057 \pm 0.005$$

Hard-Modelling



The model:

$$\dot{[A]} = -k_1[A]$$

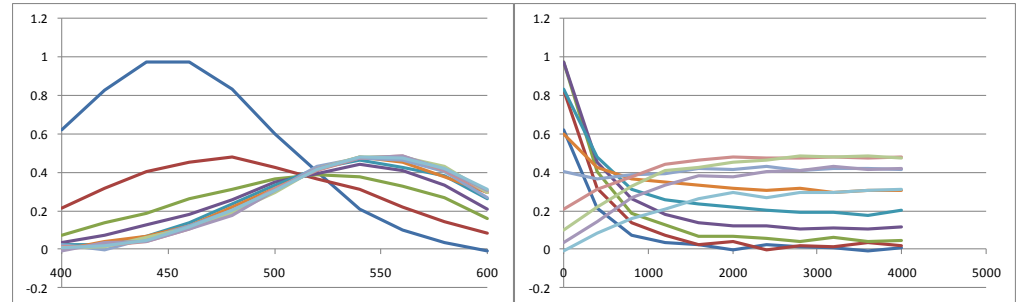
$$\dot{[B]} = k_1[A] - k_2[B]$$

$$\dot{[C]} = k_2[B]$$

↓ integration

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

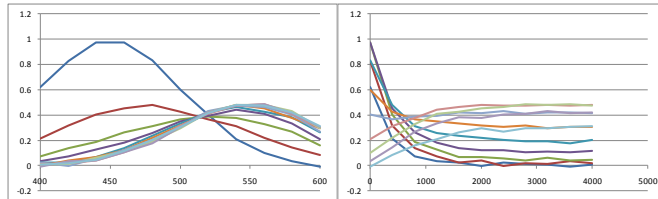


The parameters to be fitted:

- k_1, k_2
- molar absorptivities of all species at all wavelengths (e.g. $3 \times 11 = 33$)
- total 35 parameters

Difficult ?

Hard-Modelling



Fitted, using solver in excel,

- only 2 parameters, k_1 , k_2
- molar absorptivities 'eliminated'

ExcelSheet 4-5. Chapter3.xls-kinetics

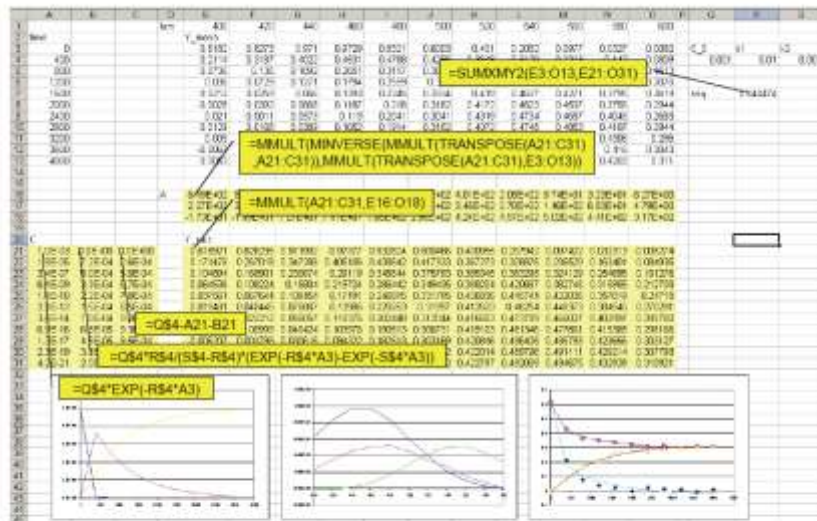


Figure 4-62. Spreadsheet for the fitting of the reaction scheme $A \rightarrow B \rightarrow C$ to multivariate data.

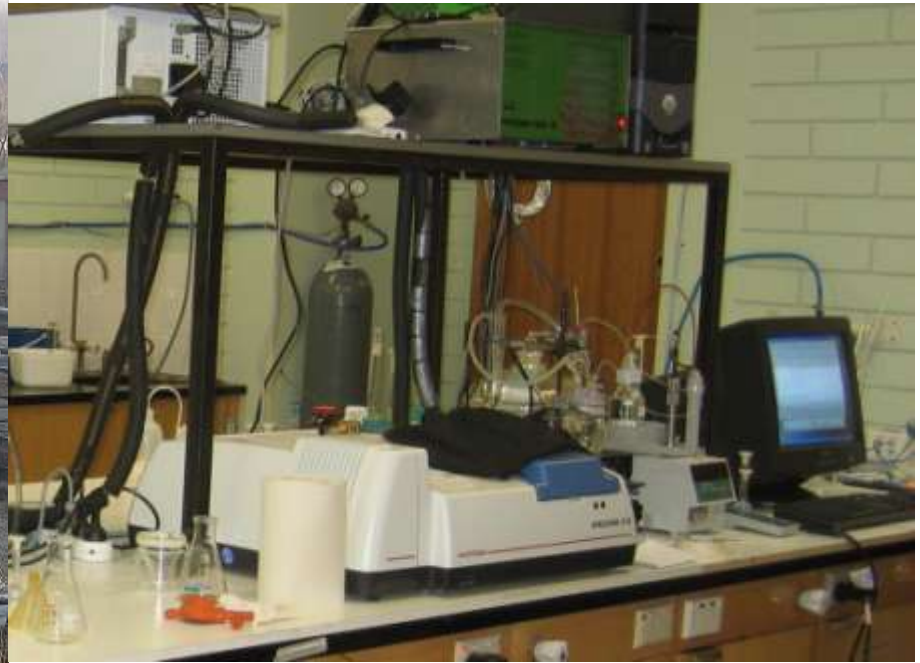


Advances in Hard-Modelling of Chemical Processes

Industry - Research Laboratory



50% reaction
50% support



1% reaction
99% support

What is left to be done in Hard-Modelling ?

Temperature Control → **thermostatting**

Ionic Strength Control → **inert salts**

pH Control → **buffers**

Temperature Control

Why do we thermostat ?

useless answer :

- to keep the temperature constant

better answer :

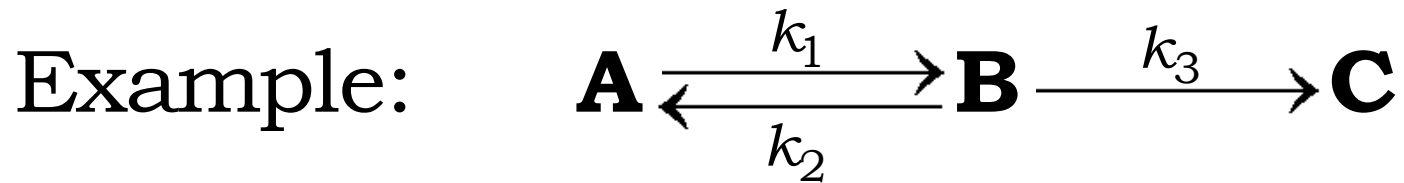
- to keep the rate constants constant

real answer :

- to keep the computations simple

Computations

How difficult is it to accommodate temperature changes during a process?



Differential equations:

$$[\dot{\mathbf{A}}] = -k_1[\mathbf{A}] + k_2[\mathbf{B}]$$

$$[\dot{\mathbf{B}}] = k_1[\mathbf{A}] - k_2[\mathbf{B}] - k_3[\mathbf{B}]$$

$$[\dot{\mathbf{C}}] = k_3[\mathbf{B}]$$

Matlab code as part of ODE solver:

```
c_dot(1,1)=-k(1)*c(1)+k(2)*c(2); % A_dot
c_dot(2,1)= k(1)*c(1)-k(2)*c(2)-k(3)*c(2); % B_dot
c_dot(3,1)= k(3)*c(2); % C_dot
```

2 very short programs do the computations

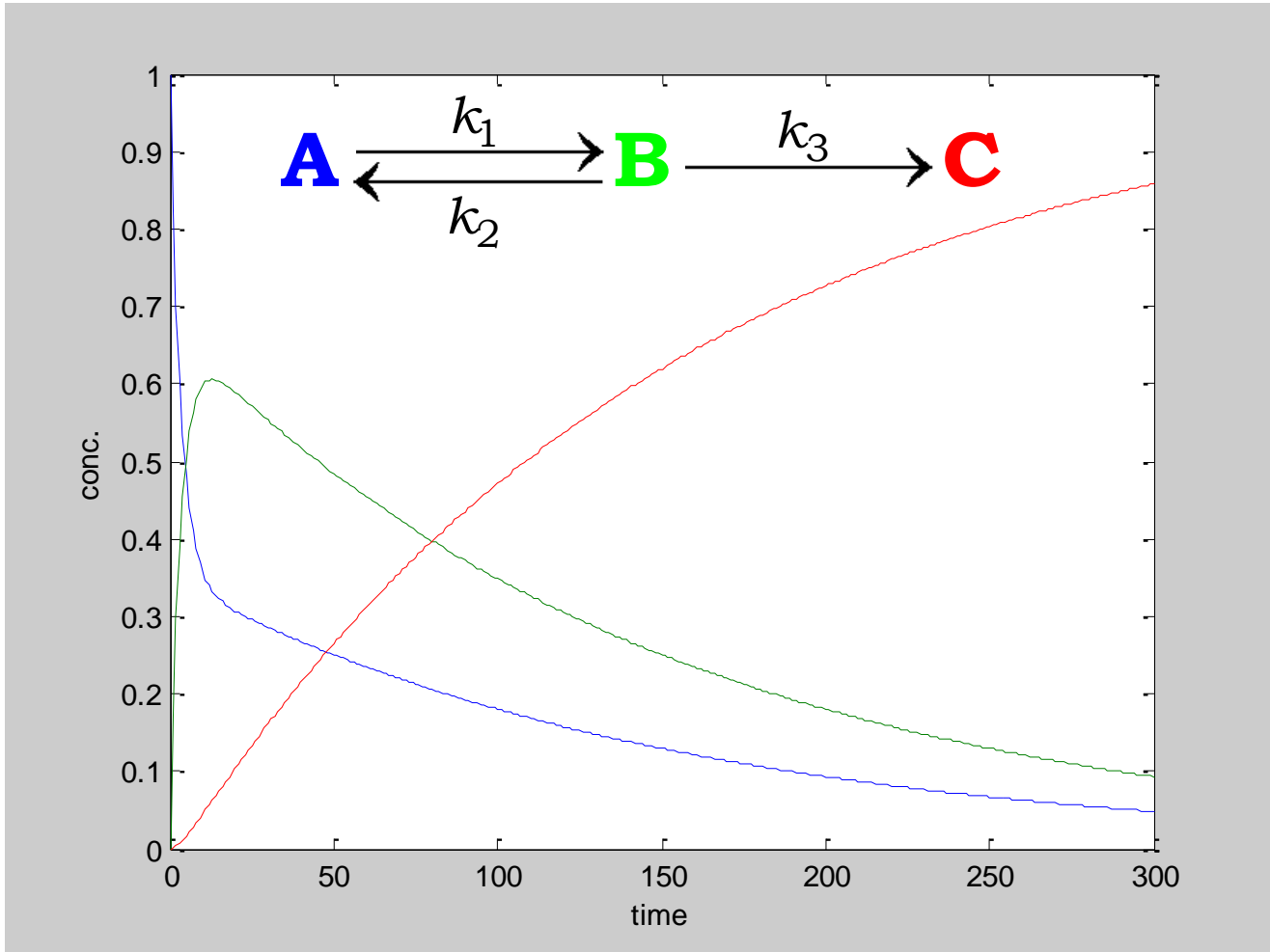
AeqBtoC.m

```
c0=[1;0;0]; % initial conc of A, Cat, B and C
k=[.2;.1;.01]; % rate constants k1 and k2
times=[0:1:300]';

[times,C] = ode45('ode_AeqBtoC',times,c0,[],k); % call ode-solver
figure(1); plot(times,C) % plotting C vs t
xlabel('time');ylabel('conc.');
```

ode_AeqBtoC.m

```
function c_dot=ode_AeqBtoC(t,c,flag,k)
% A <-> B -> C
c_dot(1,1)=-k(1)*c(1)+k(2)*c(2); % A_dot
c_dot(2,1)= k(1)*c(1)-k(2)*c(2)-k(3)*c(2); % B_dot
c_dot(3,1)= k(3)*c(2); % C_dot
```



How to accommodate temperature changes?

Arrhenius equation

Arrhenius equation describes rate constant k as a function of the temperature (**Eyring** equation could be used as well)

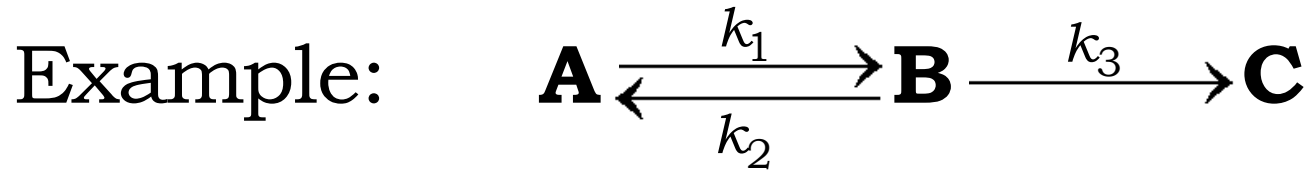
$$k = A e^{-\frac{E_a}{RT}}$$

A = pre-exponential factor

E_a = activation energy

R = gas constant (= $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = temperature in K



~~$$[\dot{A}] = -k_1[A] + k_2[B]$$~~

~~$$[\dot{B}] = k_1[A] - k_2[B] - k_3[B]$$~~

~~$$[\dot{C}] = k_3[B]$$~~

$$[\dot{A}] = -k_1(T) \times [A] + k_2(T) \times [B]$$

$$[\dot{B}] = k_1(T) \times [A] - k_2(T) \times [B] - k_3(T) \times [B]$$

$$[\dot{C}] = k_3(T) \times [B]$$

- The parameters are the Arrhenius parameters, A , E_a , not the rate constants
- The rate constants are computed using the Arrhenius parameters and the temperature
- The temperature has to be interpolated from the measured temperatures

ode_AeqBtoC_T.m

```
function c_dot=ode_AeqBtoC_T(t,c,flag,k,temp,A,Ea,times)

% A <-> B -> C

R=8.314; % gas constant J K-1 mol-1
T=lolipop(times,temp,t,2,5); % interpolation to comp T at particular time t
k=A.*exp(-Ea./(R*(T+273))); % rate constants at T

c_dot(1,1)=-k(1)*c(1)+k(2)*c(2); % A_dot
c_dot(2,1)= k(1)*c(1)-k(2)*c(2)-k(3)*c(2); % B_dot
c_dot(3,1)= k(3)*c(2); % C_dot
```

A side issue, lolipop.m

```
lolipop.m
```

```
function y1=lolipop(x,y,x1,nd,npoints)
```

```
% General Polynomial Inter/Extrapolation, degree nd, using npoints  
% x,y,x1,y1 vectors - x,y do not have to be the same length as x1,y1  
% nd: degree of polynomials  
% npoints: number of total points to define each polynomial
```

```
for i=1:length(x1)
```

```
    N=sortrows([x y abs(x-x1(i))],3); % sort x,y by abs(x-x1(i))
```

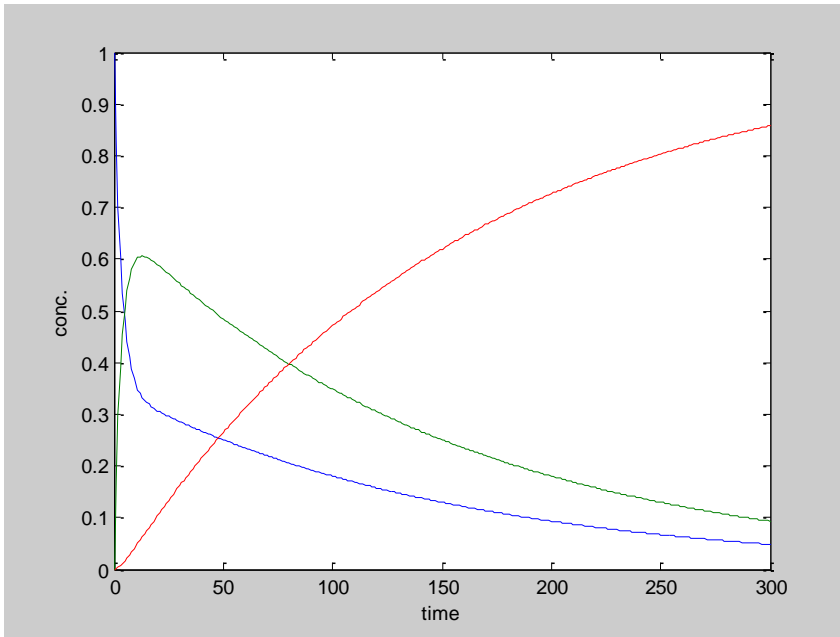
```
    x_npoints=N(1:npoints,1);          % npoints nearest nodes
```

```
    y_npoints=N(1:npoints,2);
```

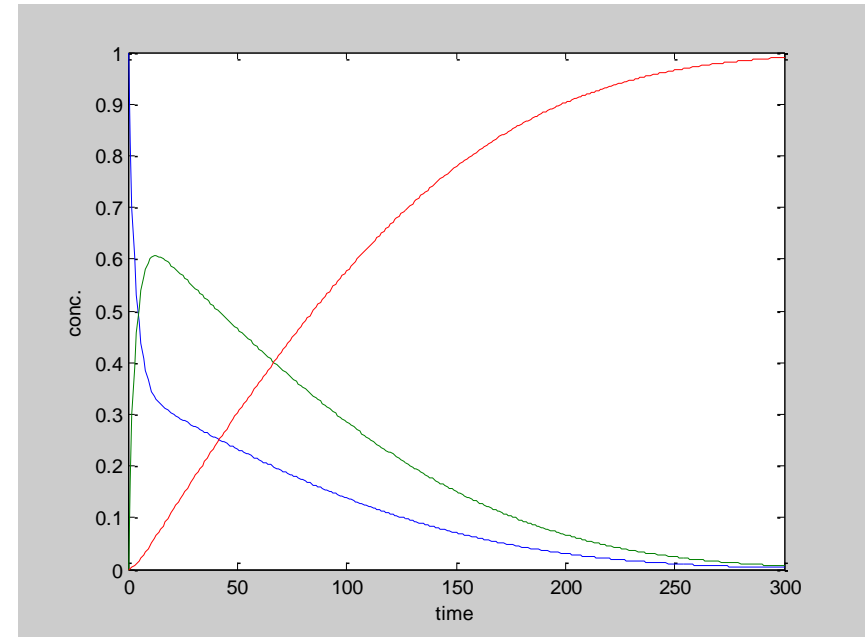
```
    a=polyfit(x_npoints-mean(x_npoints),y_npoints,nd); % polyn. par.
```

```
    y1(i)=polyval(a,x1(i)-mean(x_npoints)); % interpolate
```

```
end
```



at 20 C



at 20-80 C

Compression of process, similar to temperature program in GC
or non-isocratic mobile phase in HPLC

Cyanoacetic acid + ethanol in equilibrium with the ester

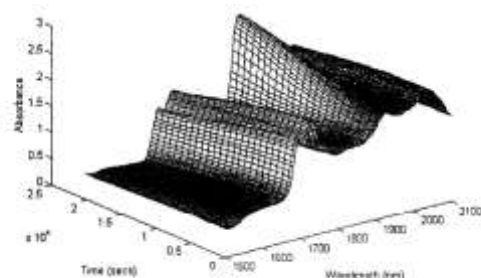


Fig. 2. A typical non-isothermal spectrophotometric measurement of the esterification reaction and absorbance as a function of time and wavelength.

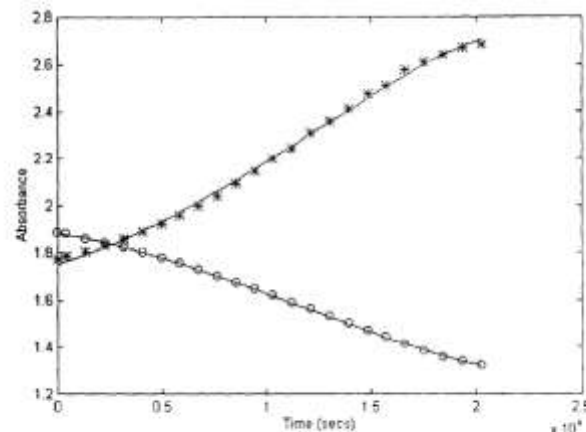
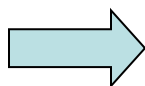


Fig. 3. Fitted curves at two representative wavelengths. The markers represent absorption measurements at 1698 nm ('x') and at 1904 nm ('o'), the solid lines are the calculated curves of best fit at these wavelengths.



Analytica Chimica Acta 337 (1997) 73–81

Analysis of non-isothermal kinetic measurements

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NON-ISOTHERMAL THERMUS DETERMINATION FOR EQUILIBRIA, MODEL 204 21

Standard deviations are shown in brackets

Data set	ΔH_{+}^{\ddagger} (kJ mol ⁻¹)	ΔS_{+}^{\ddagger} (J mol ⁻¹ K ⁻¹)
1	42.7 (0.4)	-211 (1.5)
2	39.2 (0.6)	-222 (2.1)
3	41.9 (1.0)	-214 (3.3)
4	42.5 (1.2)	-212 (4)

Activity coefficients

Why do we add inert salts ?

useless answer :

- to keep the ionic strength constant

better answer :

- to keep the rate constants constant

real answer :

- to keep the computations simple



$$[\dot{A}] = [\dot{B}] = -k_1[A][B] + k_2[C]$$

$$[\dot{C}] = +k_1[A][B] - k_2[C]$$

$$[\dot{A}] = [\dot{B}] = -k_1\{A\}\{B\} + k_2\{C\}$$

$$[\dot{C}] = +k_1\{A\}\{B\} - k_2\{C\}$$

$\{A\}$ = activity of species A

Activity coefficients

$$\{A\} = \gamma_A [A]$$

For Ionic compounds, activity coefficients γ can be approximated in reasonably dilute solutions as (Debye-Hückel):

$$\log \gamma = \frac{-A z^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

With A parameter depending on dielectric constant of solvent, in water $A \sim 0.51$

z_i charge of species

μ Ionic strength of solution, computed as:
$$\mu = \frac{1}{2} \sum_i [C_i] z_i^2$$

```

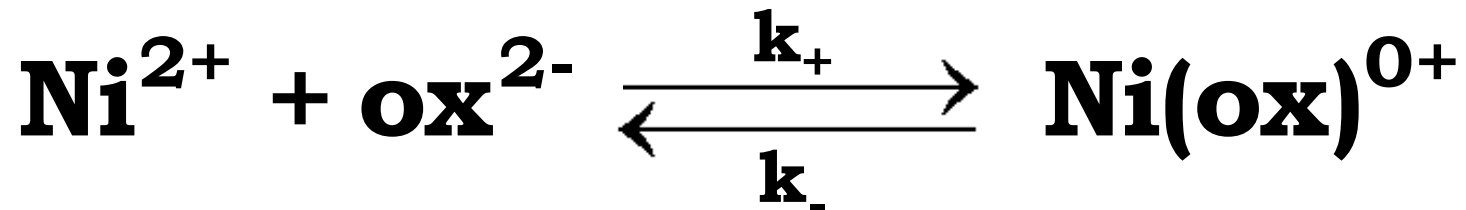
function c_dot=ode_AplusBeqC_I(t,c,flag,k,c_I,charges,mode,A)

% A + B <--> C including activities

mu          = sum(1/2*([c;c_I].*(charges.^2)));           % ionic strength
log_gamma   = (-A*(charges.^2)*(mu^0.5))/(1+(mu^0.5)); % log gamma
gamma       = 10.^log_gamma;                             % gamma
act         = c.*gamma(1:length(c));                    % activities

c_dot(1,1) = -k(1)*act(1)*act(2)+k(2)*act(3)           % A_dot
c_dot(2,1) = c_dot(1,1);                               % B_dot
c_dot(3,1) = -c_dot(1,1);                               % C_dot

```



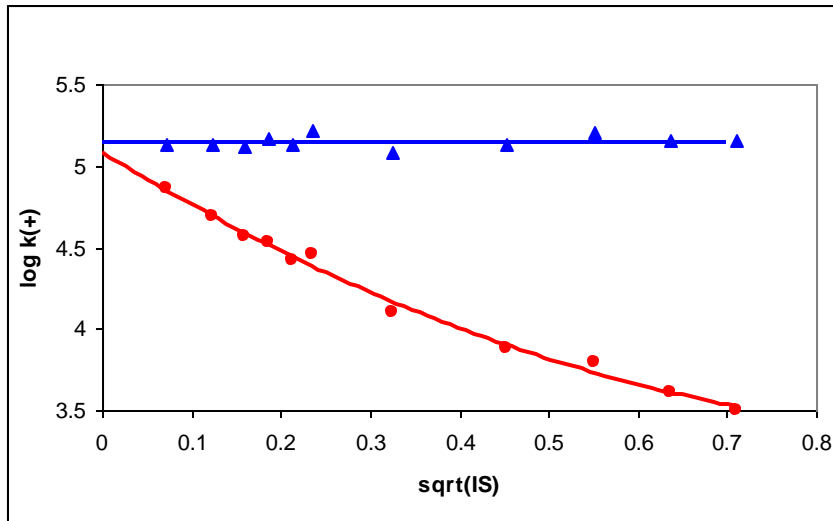
$$\begin{aligned} \frac{d[\text{Ni}^{2+}]}{dt} &= -k_+ \times \{\text{Ni}^{2+}\}\{\text{ox}^{2-}\} + k_- \times \{\text{Ni(ox)}\} \\ &= -k_+ \times \gamma_{\text{Ni}^{2+}} [\text{Ni}^{2+}] \times \gamma_{\text{ox}^{2-}} [\text{ox}^{2-}] + k_- \times [\text{Ni(ox)}] \end{aligned}$$

$\gamma_{\text{Ni}^{2+}}, \gamma_{\text{ox}^{2-}}$

continuously change as the ionic strength decreases during the reaction

$\gamma_{\text{Ni(ox)}}$ is 1, no charge

k_+ as a function of ionic strength



$$\frac{d[\text{Ni}^{2+}]}{dt} = k_+ \times \{\text{Ni}^{2+}\}\{\text{ox}^{2-}\} + k_- \times \{\text{Ni(ox)}\}$$

$$\frac{d[\text{Ni}^{2+}]}{dt} = k_+ \times [\text{Ni}^{2+}][\text{ox}^{2-}] + k_- \times [\text{Ni(ox)}]$$

k_- is not μ -dependent, as Ni(ox) has no charge

pH control

Why do we add buffers ?

useless answer :

- to keep the pH constant

better answer :

- to keep the rate constants constant

real answer :

- to keep the computations simple

No Matlab files today,
they are too complex to be
discussed here.

Application:

saving the planet by absorbing
CO₂ from power plants,
post combustion capture PCC

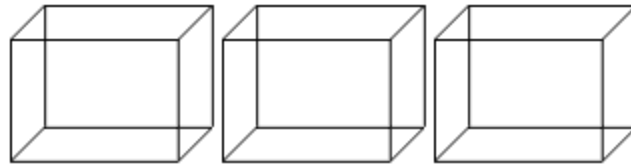
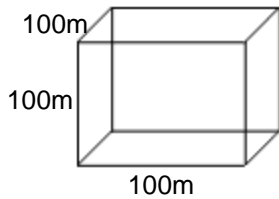
The Scale of the Problem

The mass of CO₂ produced by human activities (~25Gt/y as CO₂; ~7Gt/y carbon) is about the same as the mass of *everything* else produced by humans (including waste) put together.

CO₂ output of power station

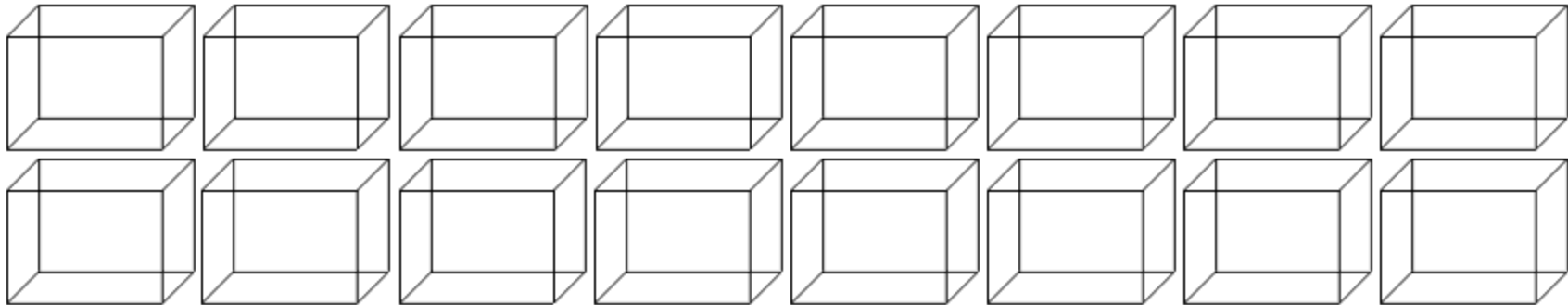
11.8 × 10⁶ t/y

33000 t/d = 4.4 × 10⁶ m³/d



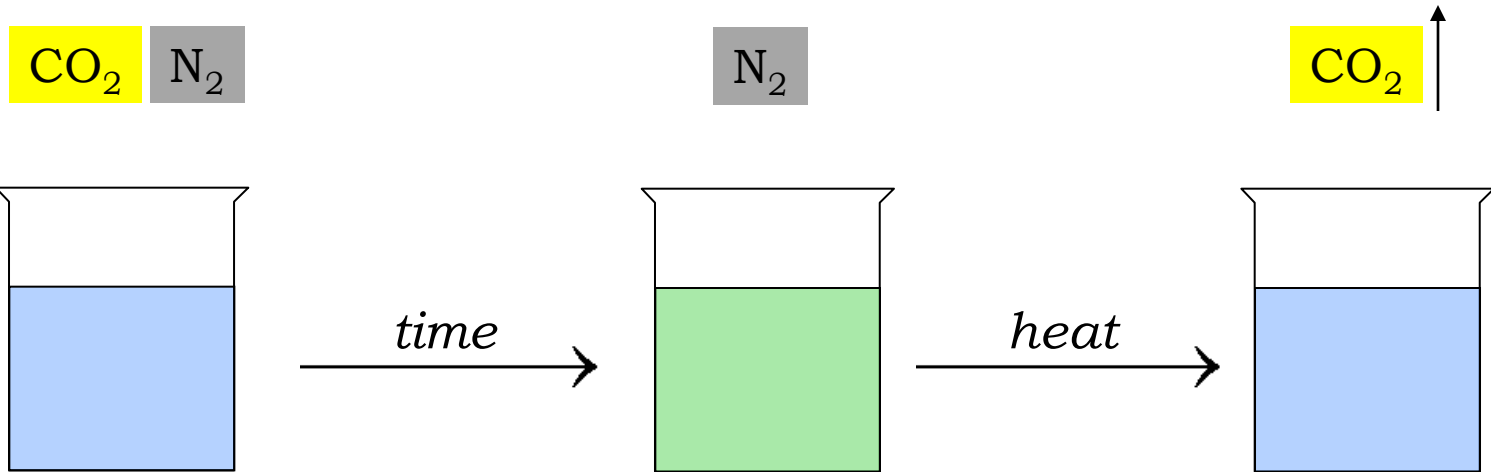
CO₂ / day

+



N₂

The Principle of PCC



base,

~~e.g. NaOH~~

~~Na_2CO_3~~

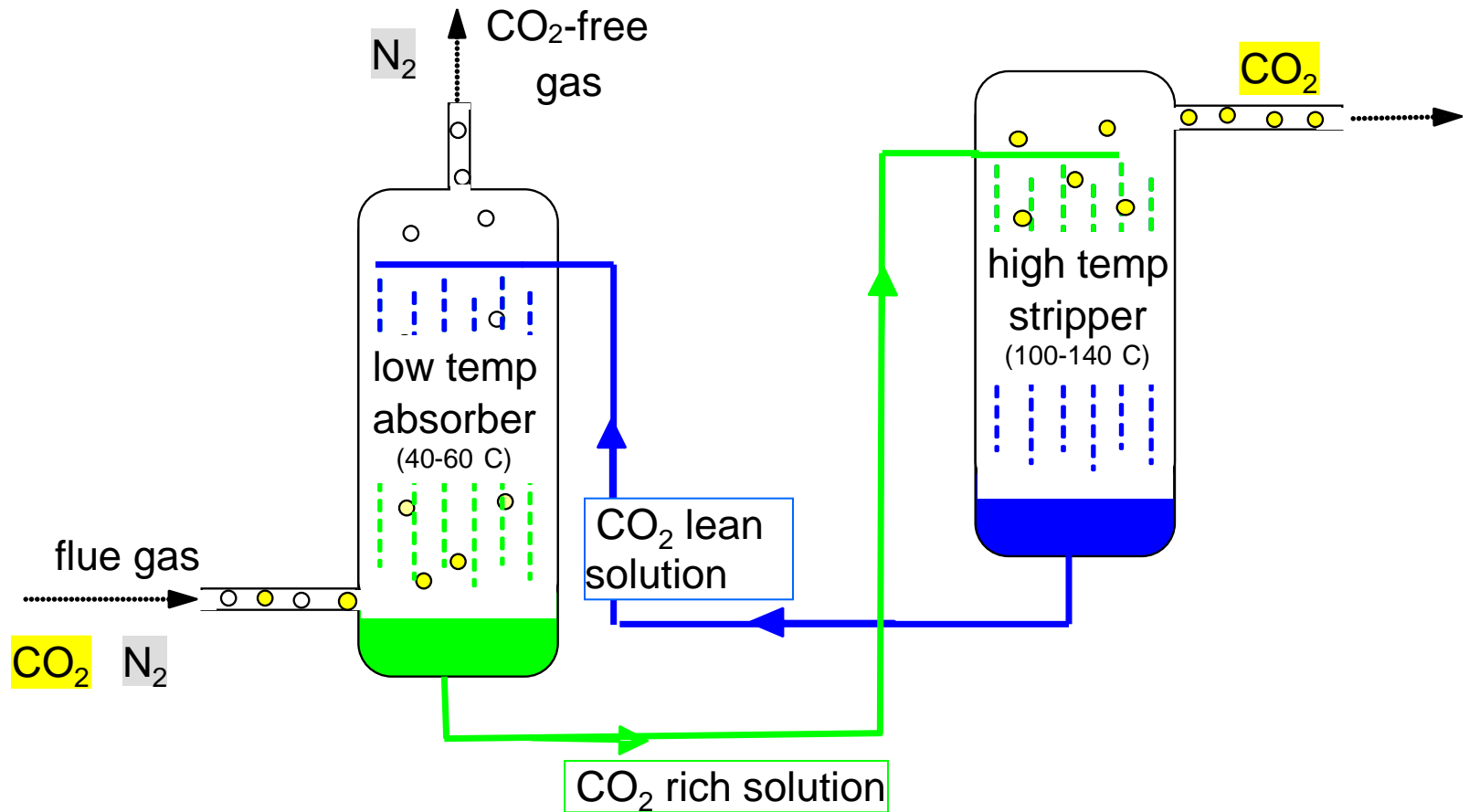
~~NaOH~~

or better R-NH_2

RNH_3^+ , HCO_3^-

R-NH_2

schematic diagram of PCC plant



First questions a chemist is asking:

- What are the molecules that interact in PCC ?
- How do they interact with each other ?

What are the molecules that interact in PCC ?

{CO₂}

CO₂(aq), H₂CO₃
HCO₃⁻, CO₃²⁻

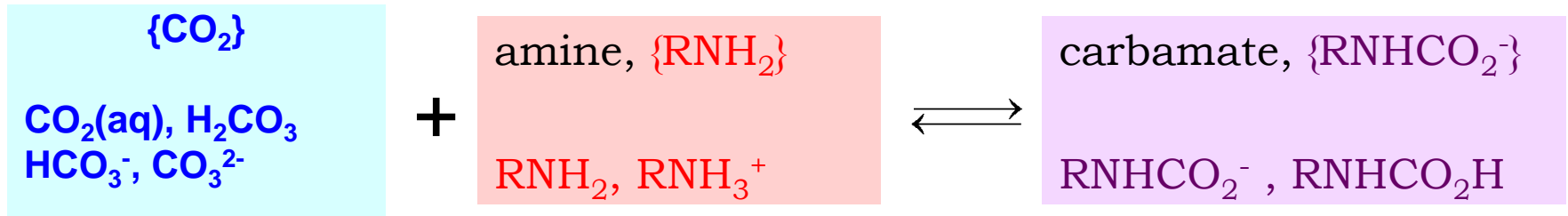
amine, **{RNH₂}**

RNH₂, RNH₃⁺

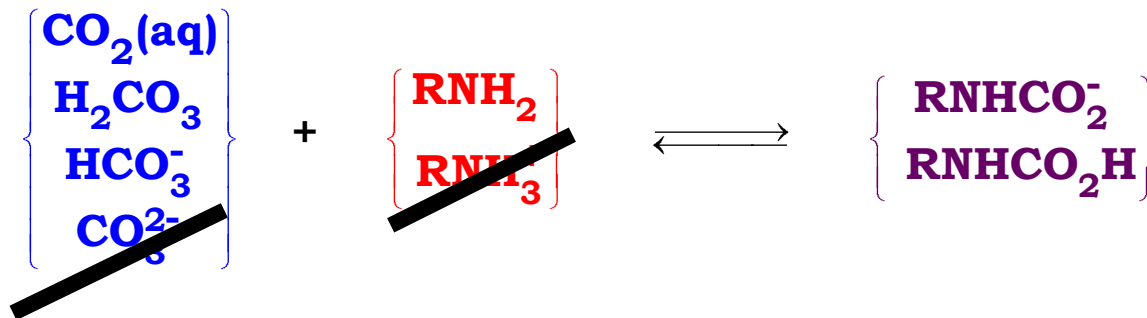
carbamate, **{RNHCO₂⁻}**

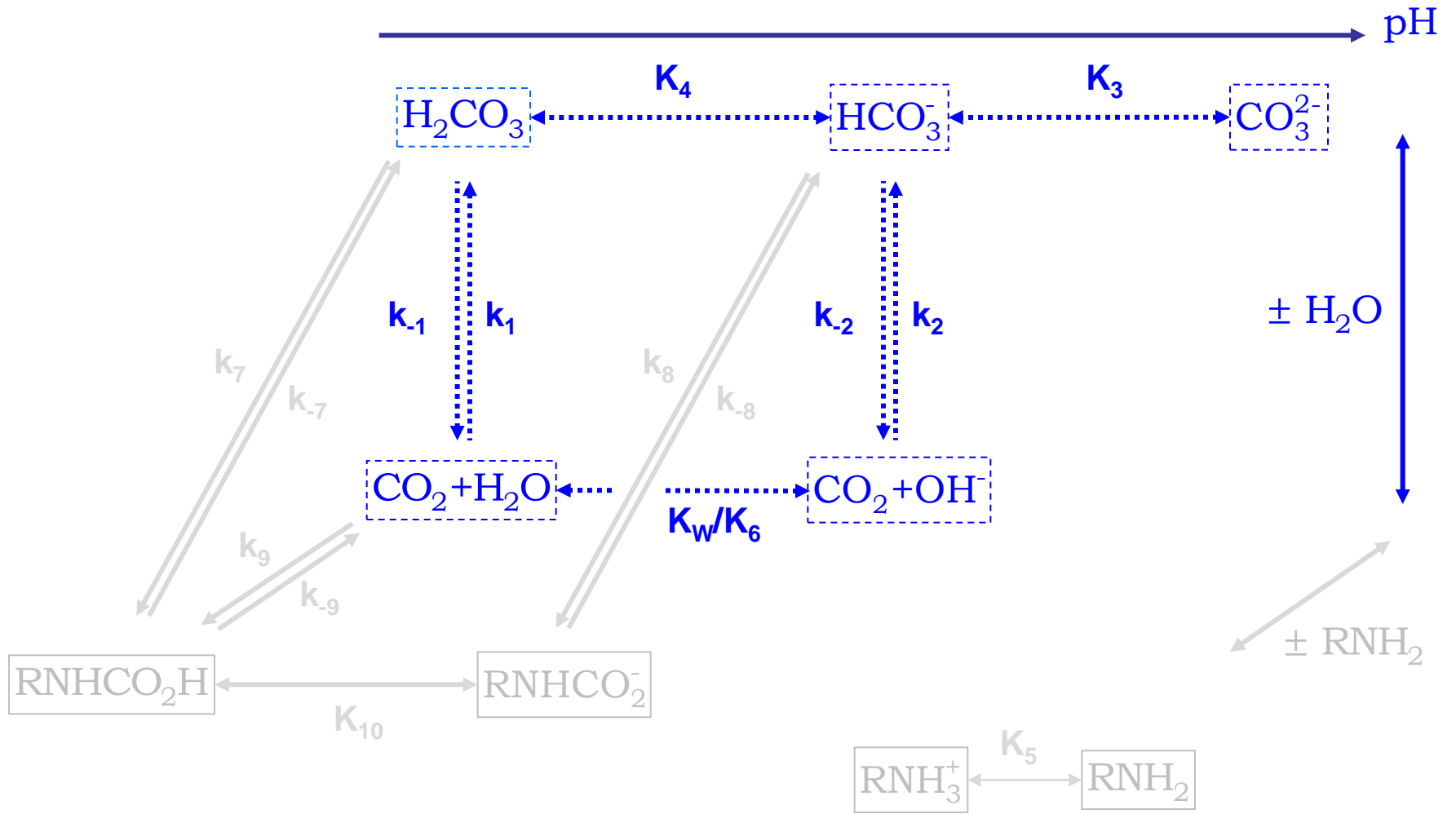
RNHCO₂⁻, RNHCO₂H

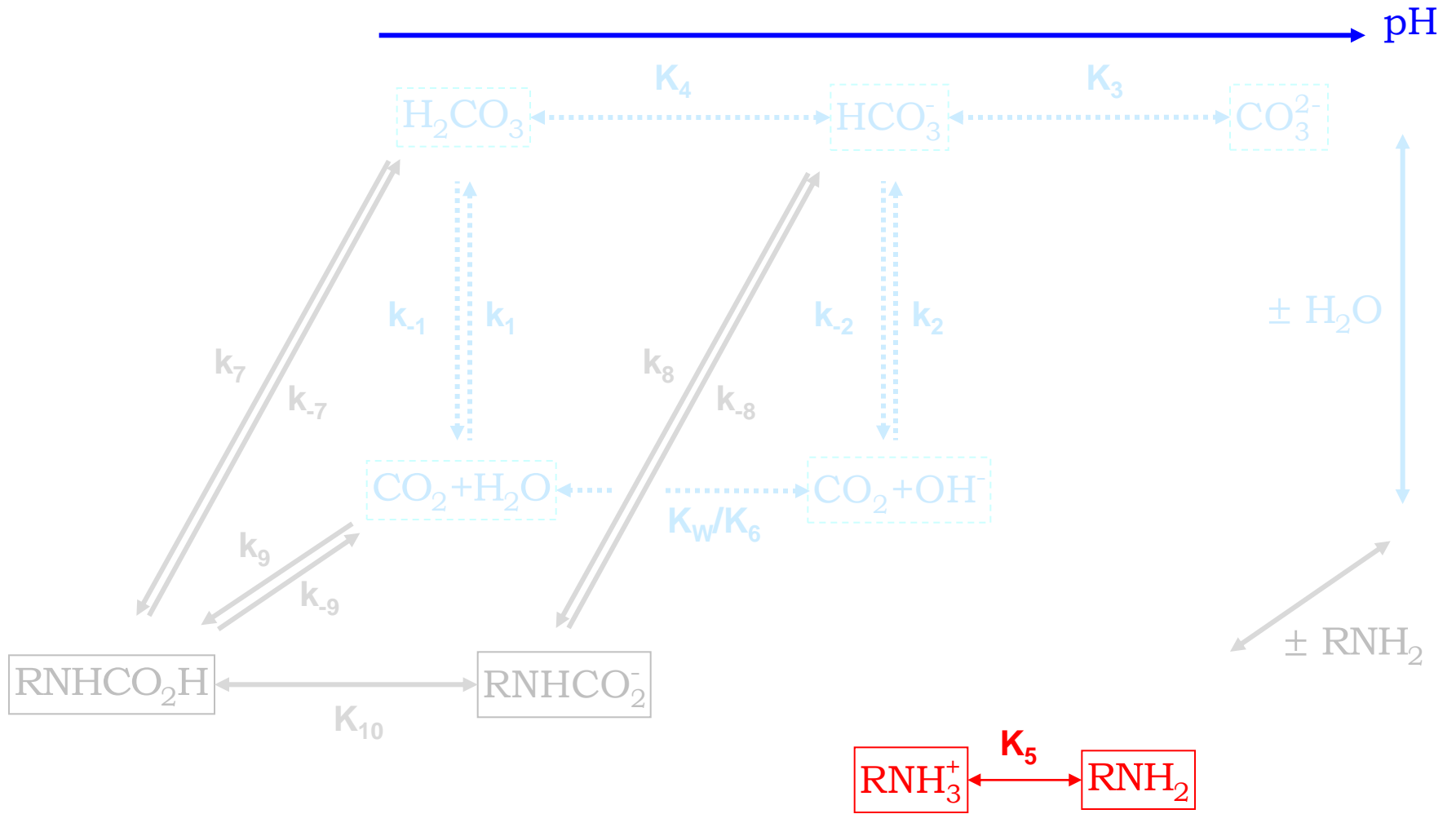
How is the carbamate formed?

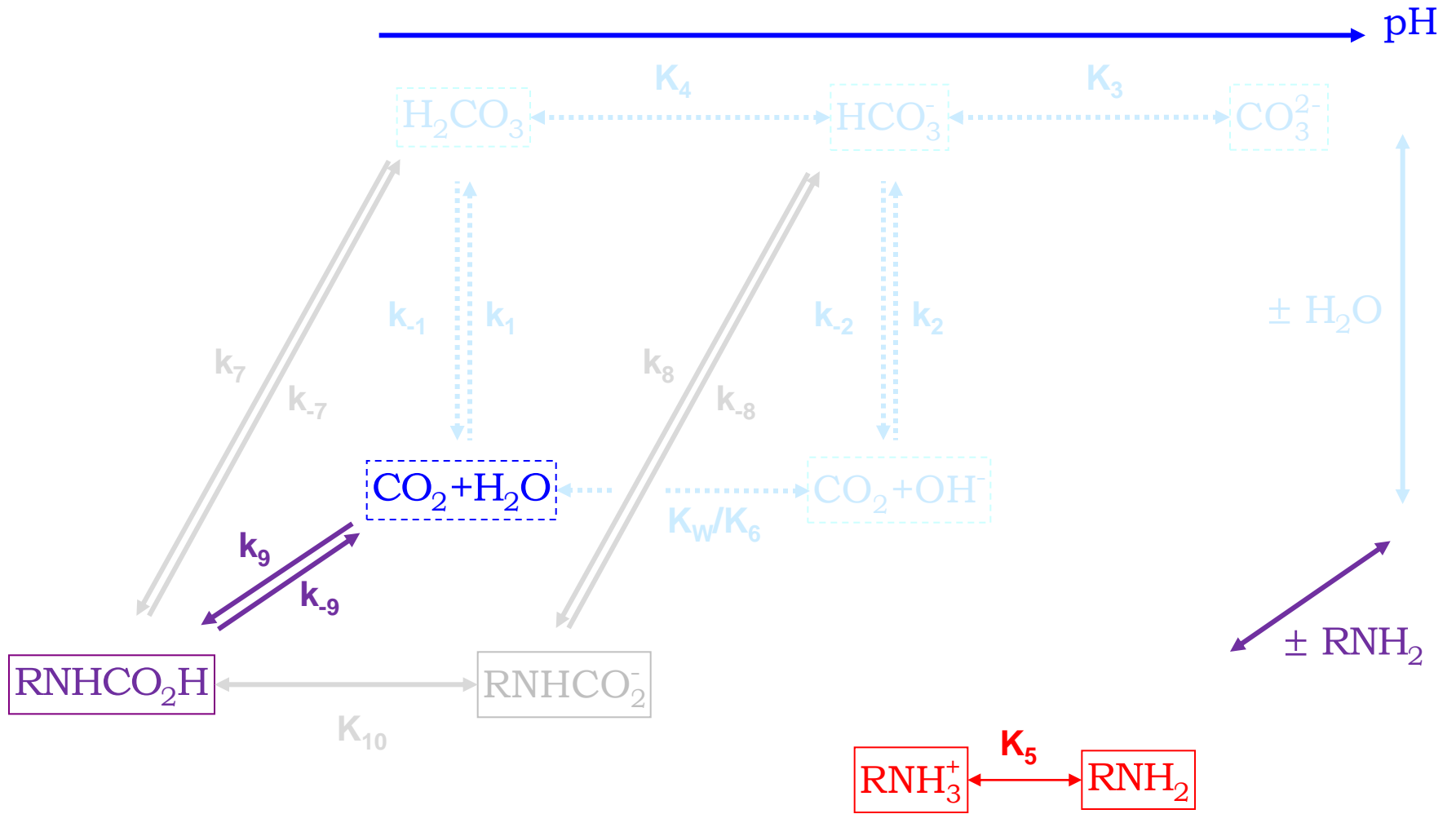


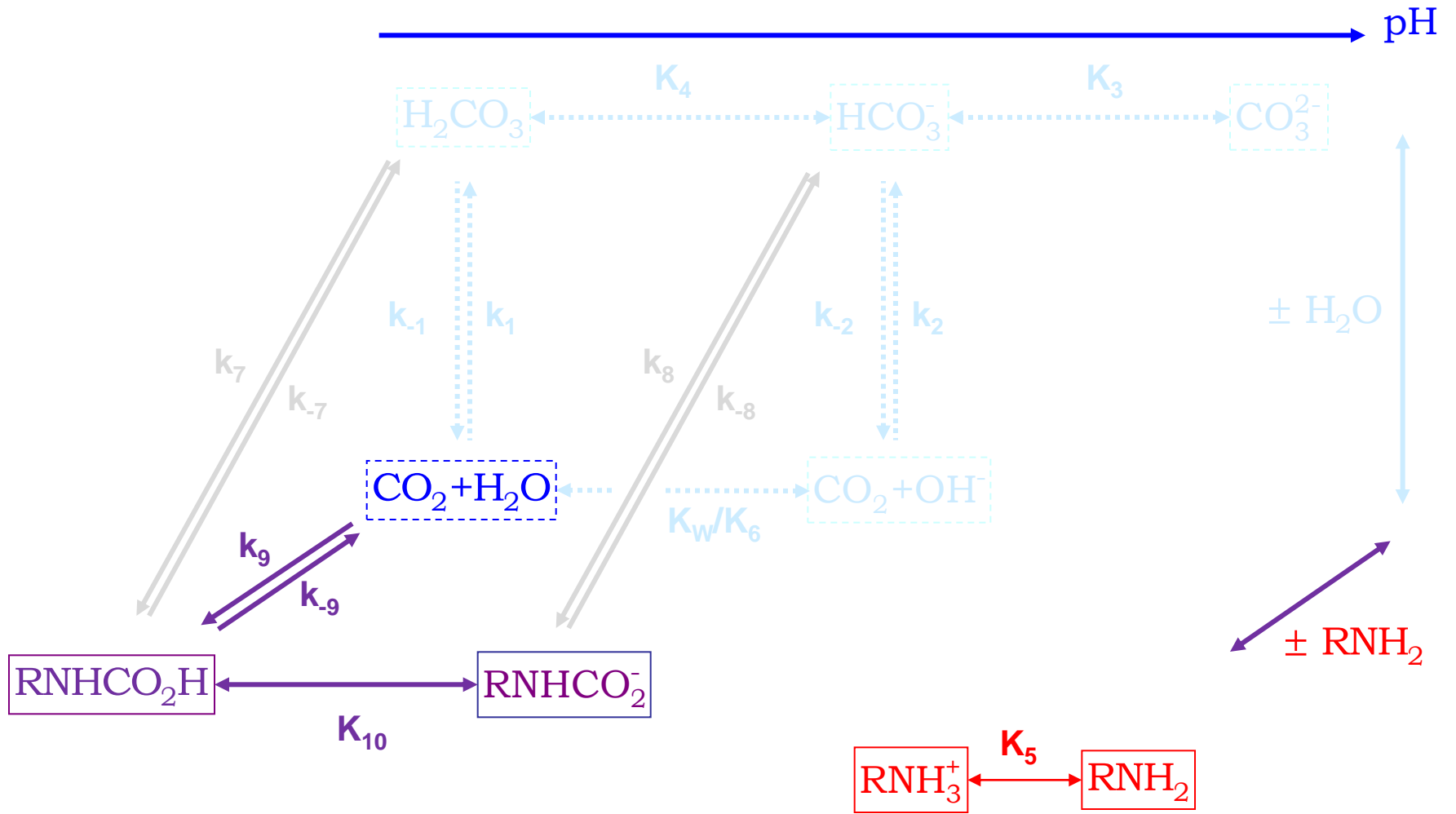
1 molecule + **1 molecule** ⇌ **1 molecule**

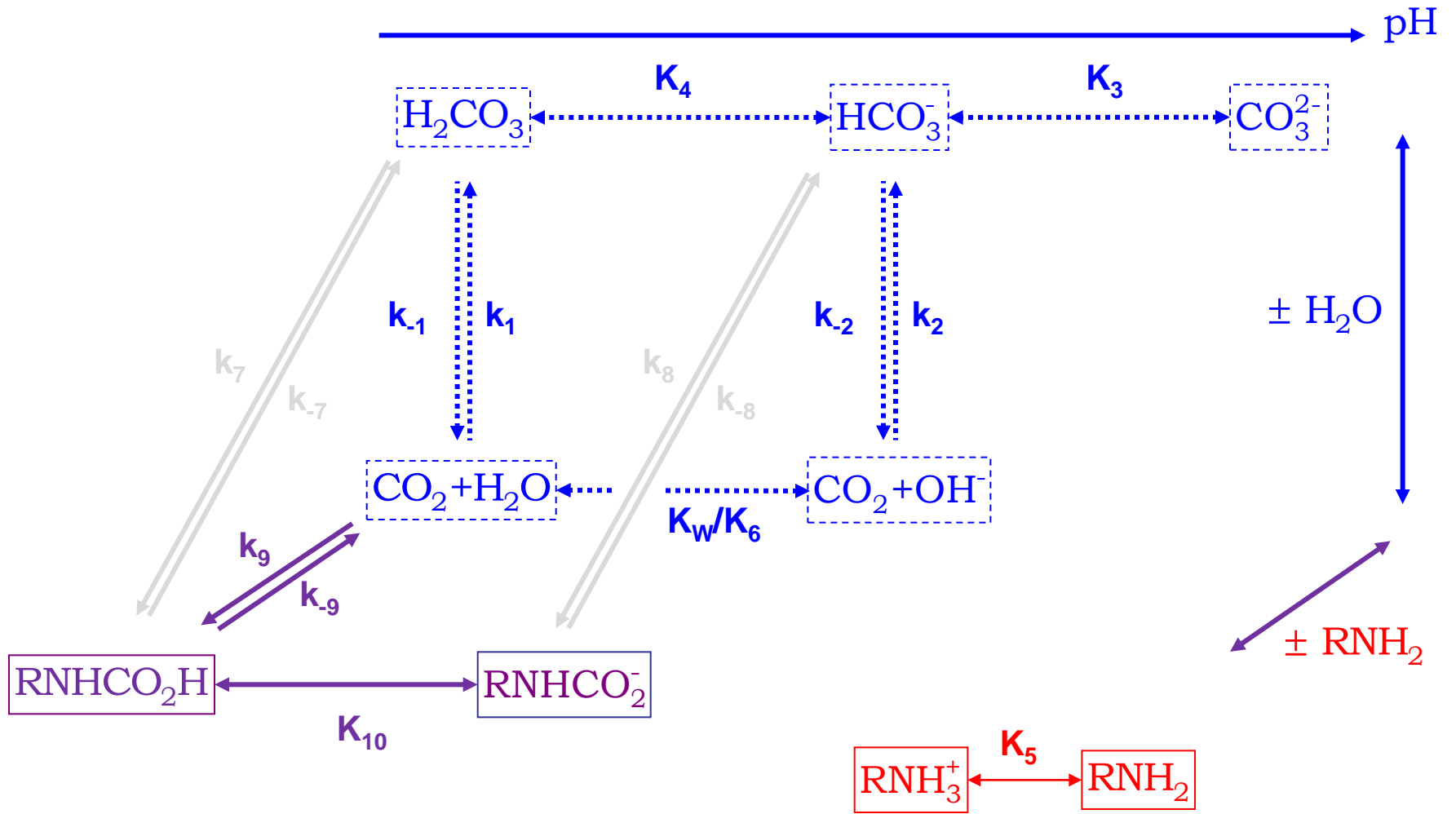


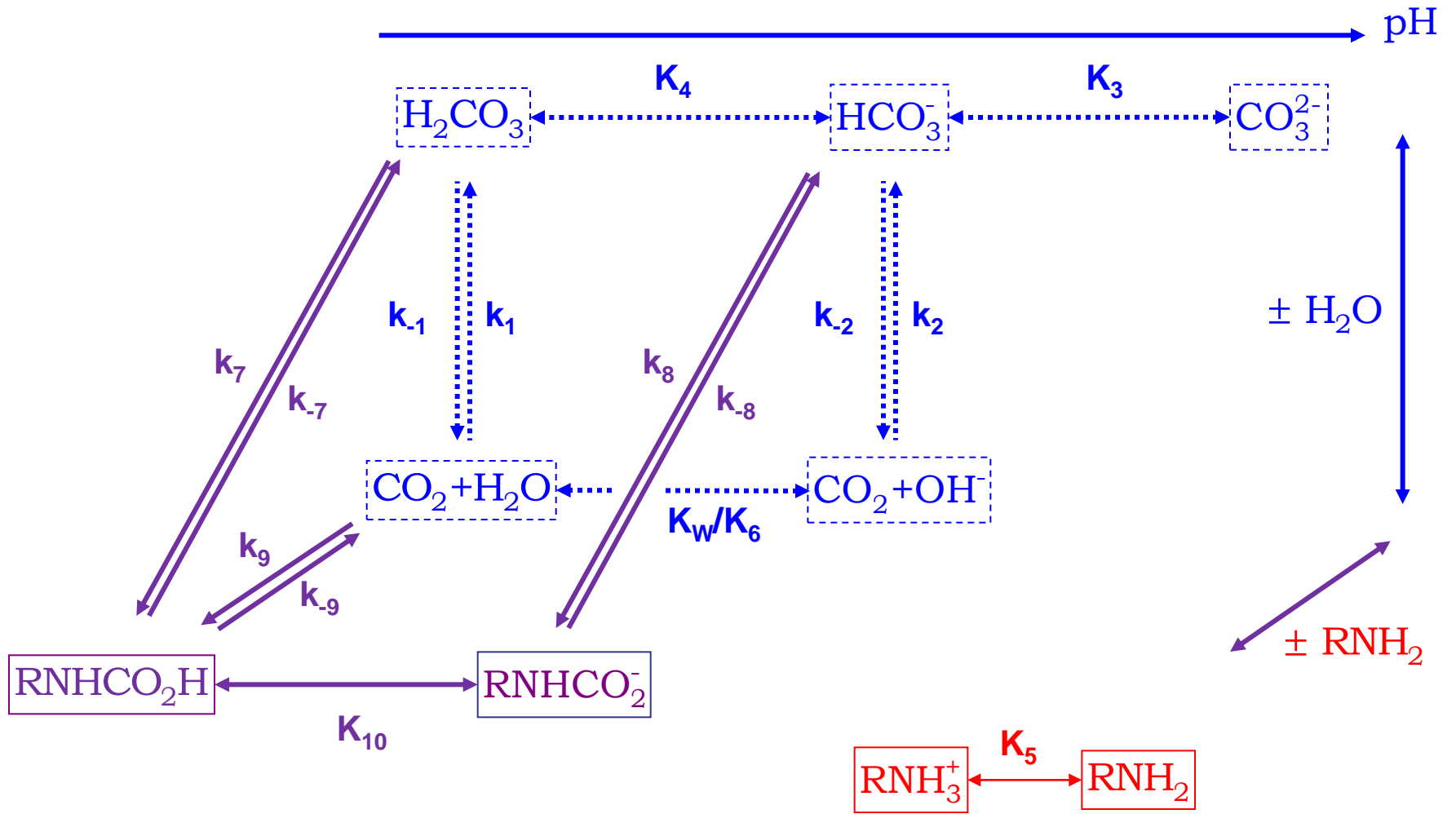




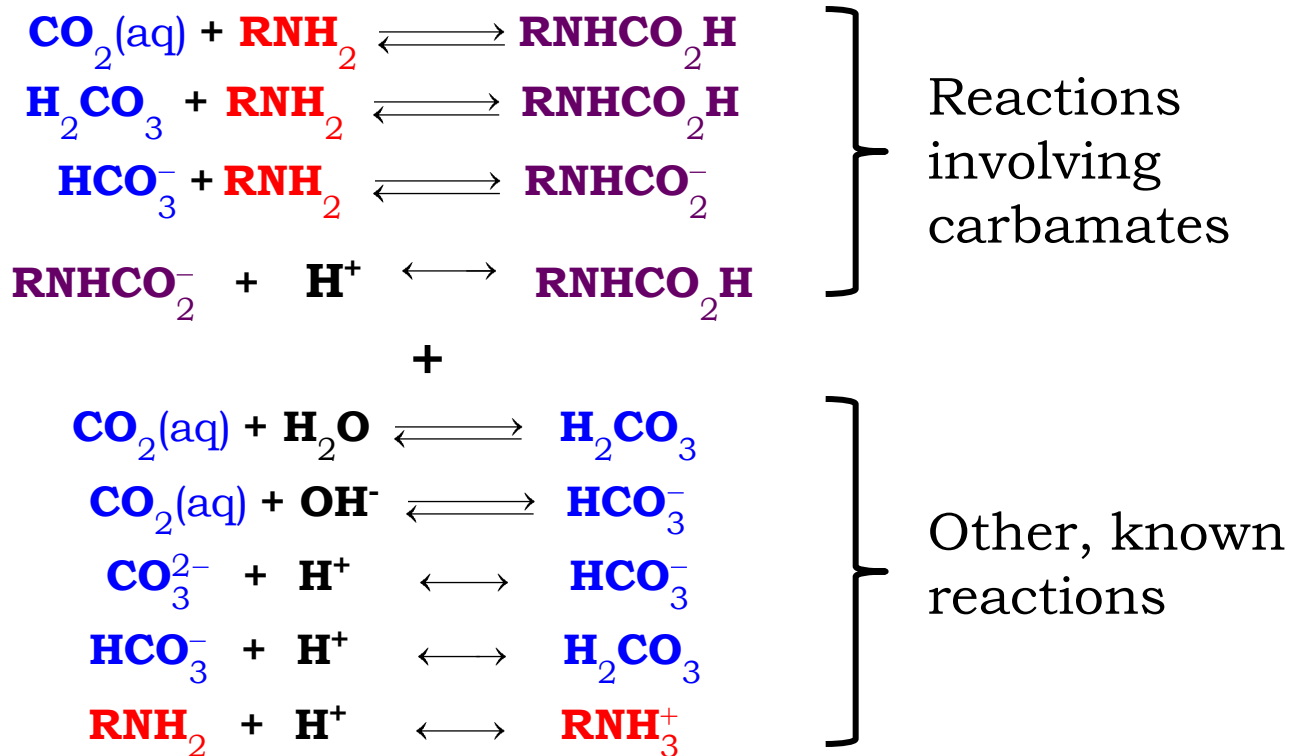








The complete reaction scheme



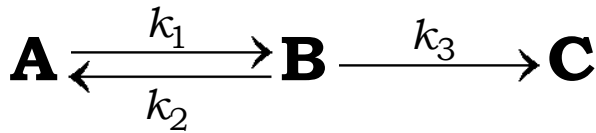
To be determined:

- 6 rate constants
- 1 equilibrium constants
- - 3 due to microscopic reversibility

Measurement techniques

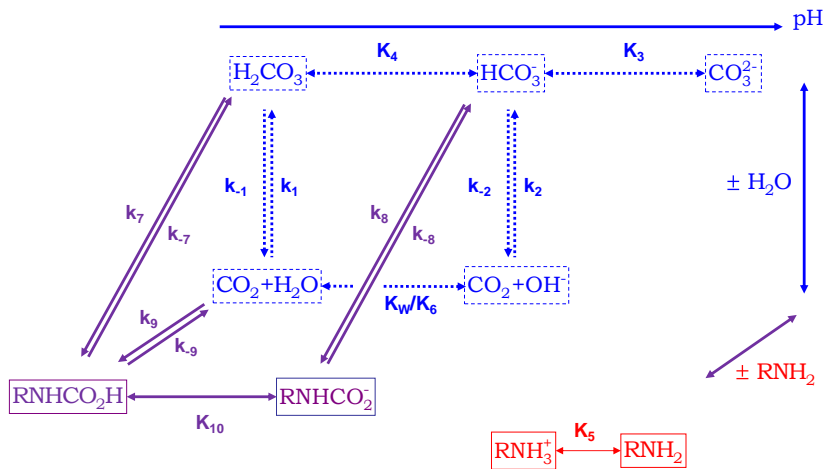
- $p(\text{CO}_2)$ partial pressure in gas phase (slow)
- $\text{Ba}(\text{CO}_3)$ precipitation (slow)
- Conductometry (fast, not specific)
- **pH, indicator (fast)**
- NMR
 - ^{13}C -NMR (slow, not quantitative)
 - **^1H -NMR (intermediate, quantitative)**

Side issue: translation of model into Matlab code



```

c_dot(1,1)=-k(1)*c(1)+k(2)*c(2); % A_dot
c_dot(2,1)= k(1)*c(1)-k(2)*c(2)-k(3)*c(2); % B_dot
c_dot(3,1)= k(3)*c(2); % C_dot
    
```



User interface based on Excel, model parser

Define and Compile Model

Reactants	Reaction Type	Products	Parameter Value	±	Fit / Fix
H2CO3	>	CO2	1.80E+01		fix
CO2	>	H2CO3	3.70E-02		fix
HCO3	>	CO2+OH	2.38E-04		fix
CO2+OH	>	HCO3	8.50E+03		fix
A+H2CO3	>	ACO2H	2.17E+02	4.97E+00	fit
ACO2H	>	A+H2CO3	6.23E-03	2.76E-04	fit
A+HCO3	>	ACO2	9.80E-05	5.41E-06	fit
ACO2	>	A+HCO3	1.02E-05		fix
CO3+H	=	HCO3	1.03E+01		fix
CO3+2H	=	H2CO3	1.41E+01		fix
A+H	=	AH	9.35E+00		fix
ACO2+H	=	ACO2H	7.32E+00		fix

calculated

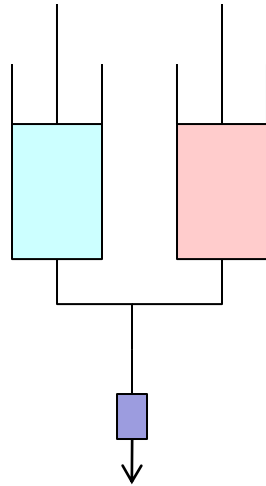
calculated

Example 1:

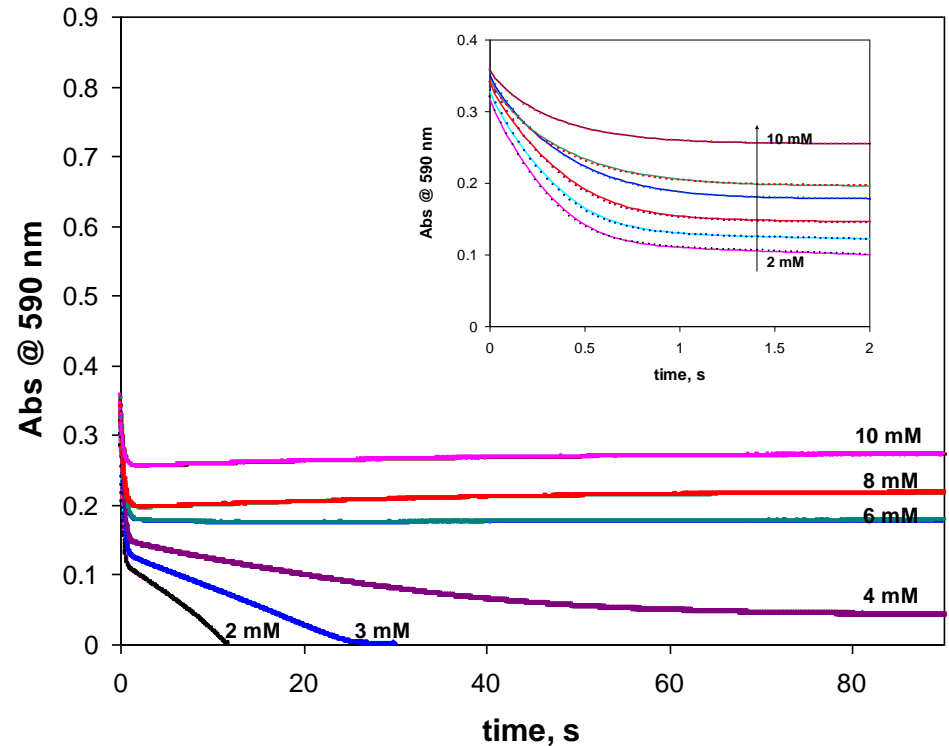
Ammonia, NH_3

Measurements, stopped-flow

$[\text{CO}_2] = 3.8 \text{ mM}$

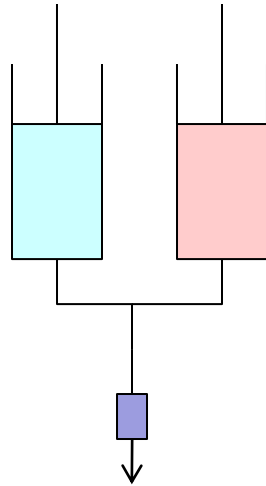


$[\text{NH}_3] = 2\text{-}10 \text{ mM}$
 $[\text{ThB}] = 12.5 \text{ }\mu\text{M}$



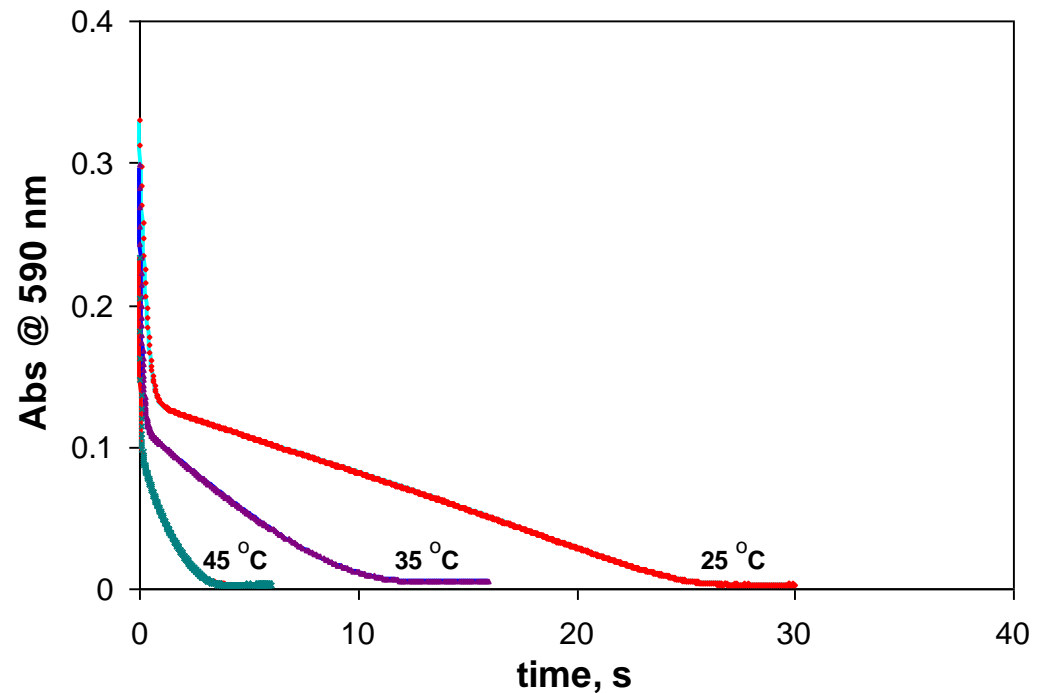
Measurements, stopped-flow

$[\text{CO}_2] = 3.8 \text{ mM}$

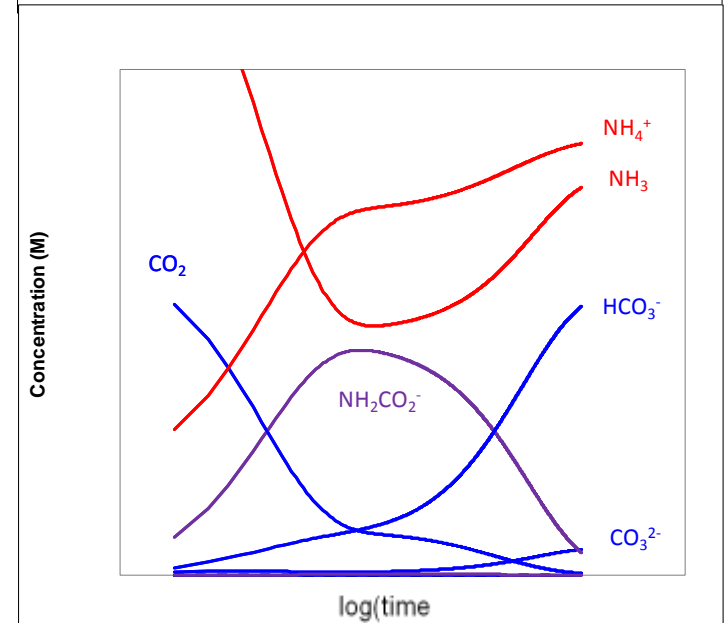
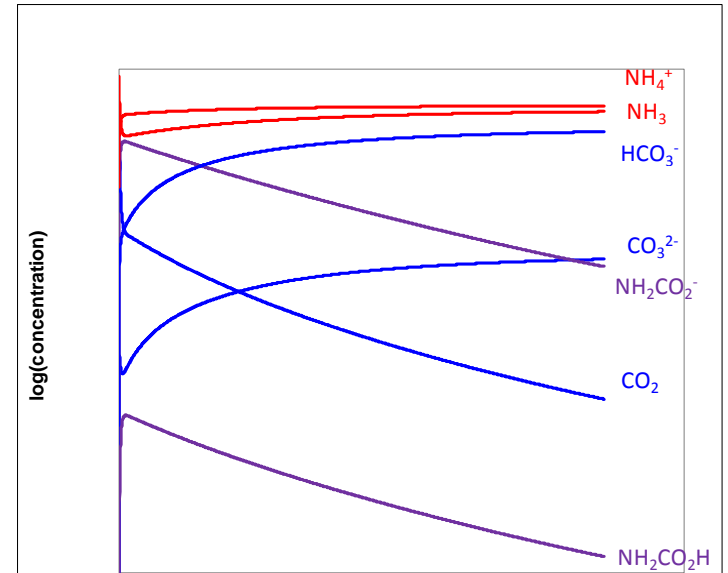
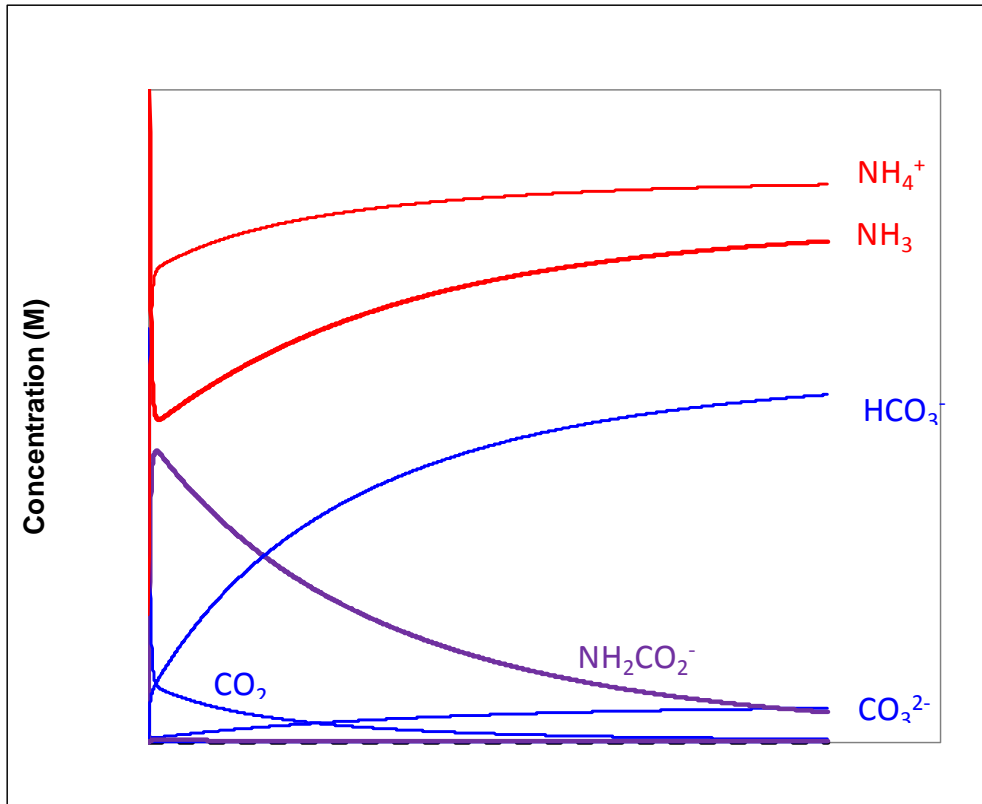


$[\text{NH}_3] = 3 \text{ mM}$
 $[\text{ThB}] = 12.5 \text{ }\mu\text{M}$

different temp.



Analysis: $\text{NH}_3 + \text{CO}_2$

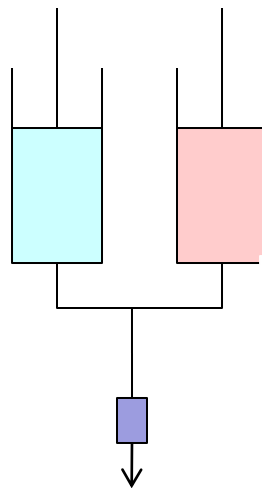


Measurements, stopped-flow

$[\text{NH}_3] = 44 \text{ mM}$
 $[\text{HCO}_3^-] = 94 \text{ mM}$

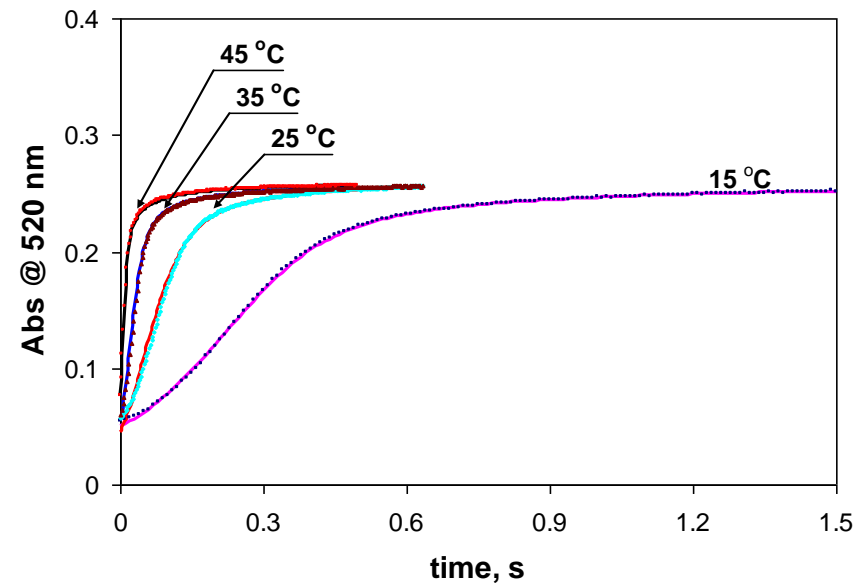
equilibration

$[\text{NH}_3] = \dots \text{ M}$
 $[\text{HCO}_3^-] = \dots \text{ M}$
 $[\text{NH}_2\text{COO}^-] = \dots \text{ M}$

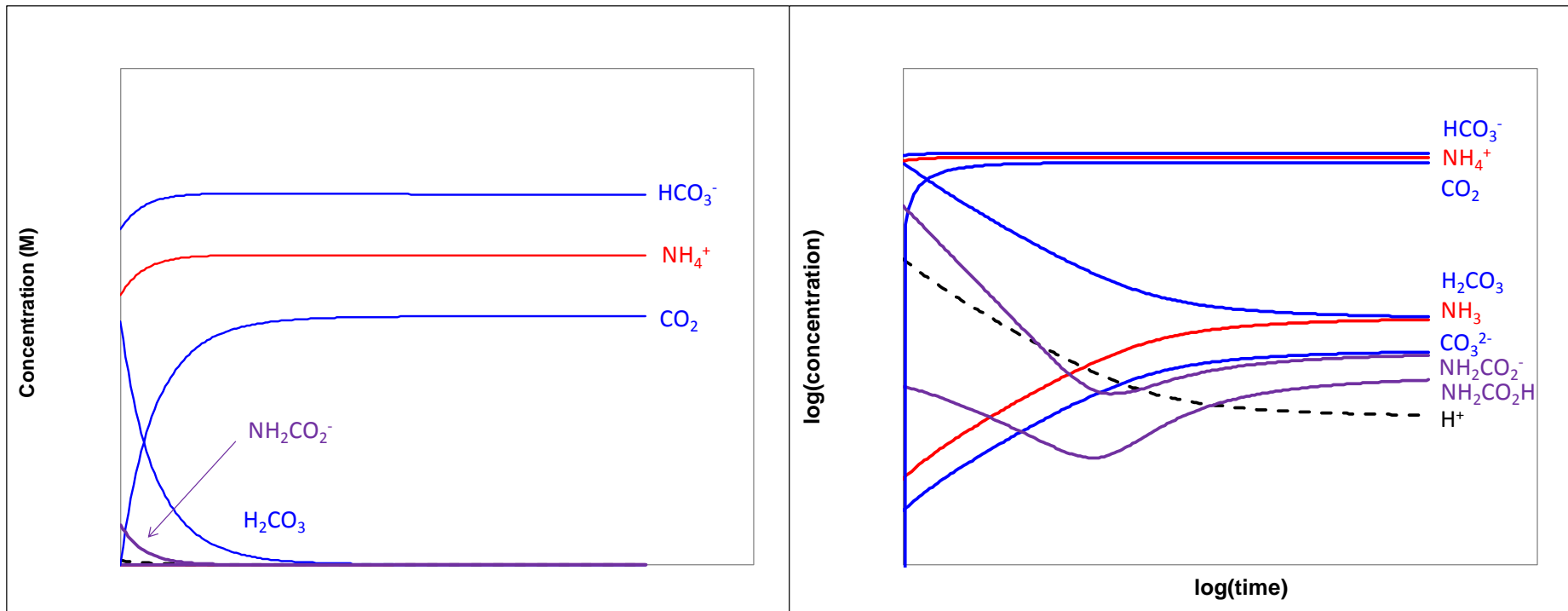


$[\text{HCl}] = 65 \text{ mM}$
 $[\text{BTB}] = 12 \mu\text{M}$
 $[\text{AlRed}] = 50 \mu\text{M}$

different temp



Analysis: $\text{NH}_2\text{COO}^- + \text{H}^+$



Very important aspect:
**all measurements were analysed
together,
global analysis!**

**There are no experimental conditions
where one experiment contains sufficient
information for a fit of the model.**

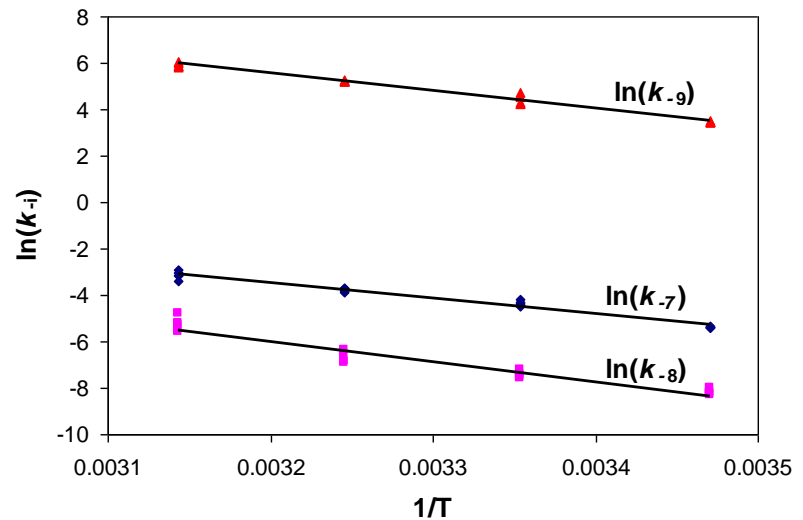
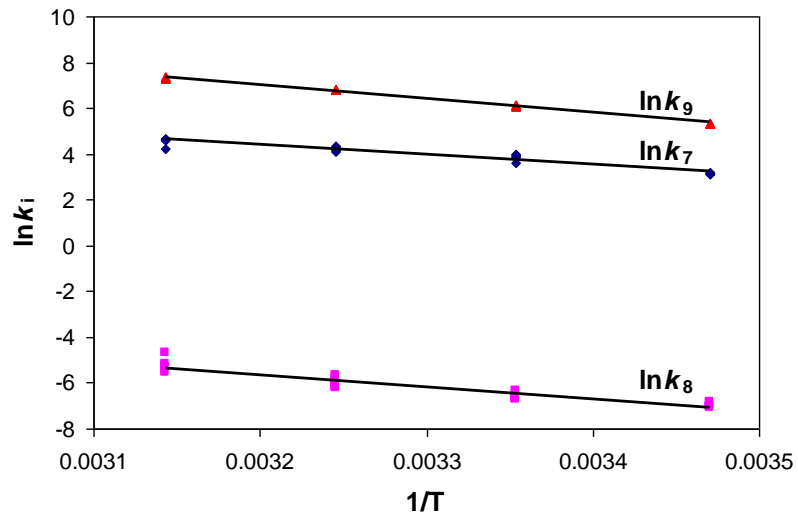
The Results:

rate and equilibrium constants as a function of the temperature

T [°C]	k_7 [M ⁻¹ s ⁻¹]	k_{-7} [s ⁻¹]	k_8 [M ⁻¹ s ⁻¹]	k_{-8} [s ⁻¹]	k_9 [M ⁻¹ s ⁻¹]	k_{-9} [s ⁻¹]	$\log K_{10}$
15.0	23.5(3)	$4.6(1) \times 10^{-3}$	$9.3(9) \times 10^{-4}$	$2.8(3) \times 10^{-4}$	$2.07(1) \times 10^2$	32.2(5)	6.71(2)
25.0	49(6)	$1.3(1) \times 10^{-2}$	$1.4(2) \times 10^{-3}$	$6.0(9) \times 10^{-4}$	$4.5(1) \times 10^2$	84(16)	6.73(7)
35.0	69(5)	$2.3(1) \times 10^{-2}$	$2.5(6) \times 10^{-3}$	$1.3(3) \times 10^{-3}$	$9.25(4) \times 10^2$	$1.88(5) \times 10^2$	6.70(2)
45.0	97(14)	$4.4(7) \times 10^{-2}$	$6(2) \times 10^{-3}$	$5(1) \times 10^{-3}$	$1.53(6) \times 10^3$	$3.8(3) \times 10^2$	6.88(4)

T [°C]	K_7 [M ⁻¹]	K_8 [M ⁻¹]	K_9 [M ⁻¹]
15.0	$5.1(1) \times 10^3$	3.3(1)	6.4(1)
25.0	$3.7(6) \times 10^3$	2.29(4)	5.6(9)
35.0	$3.0(1) \times 10^3$	2.02(3)	4.9(1)
45.0	$2.2(2) \times 10^3$	1.05(5)	4.0(3)

The Results: Arrhenius and van t'Hoff plots

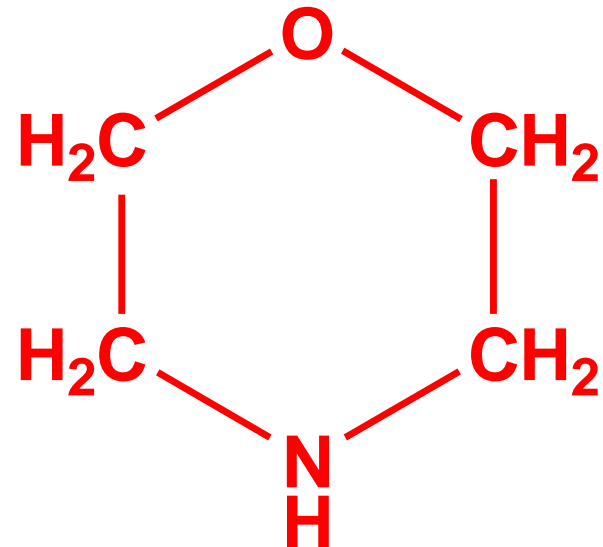


The Results: complete set of thermodynamic parameters

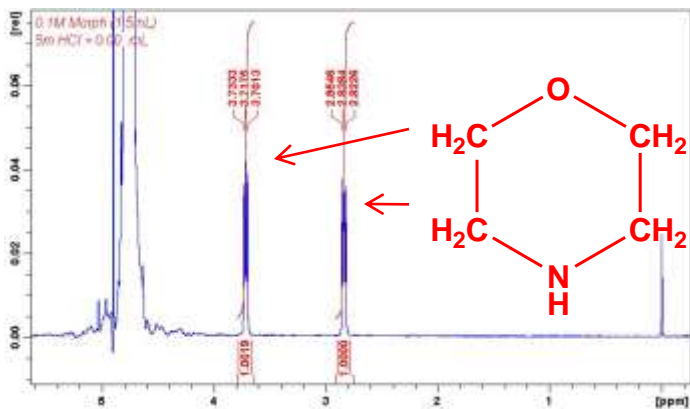
	Arrhenius		Eyring		van't Hoff	
	E_a [kJ mol ⁻¹]	A	ΔH^\ddagger [kJ mol ⁻¹]	ΔS^\ddagger [J mol ⁻¹ K ⁻¹]	ΔH^\ominus [kJ mol ⁻¹]	ΔS^\ominus [J mol ⁻¹ K ⁻¹]
$\text{NH}_3 + \text{H}_2\text{CO}_3 \xrightarrow{k_7} \text{NH}_2\text{COOH} + \text{H}_2\text{O}$	35(2)	6.0×10^7	33(2)	-104(7)	-21(2)	-1(5)
$\text{NH}_2\text{COOH} + \text{H}_2\text{O} \xrightarrow{k_{-7}} \text{H}_2\text{CO}_3 + \text{NH}_3$	56(2)	6.9×10^7	53(2)	-103(7)		
$\text{NH}_3 + \text{HCO}_3^- \xrightarrow{k_8} \text{NH}_2\text{COO}^- + \text{H}_2\text{O}$	45(4)	1.2×10^5	42(4)	-156(12)	-27(2)	-84(7)
$\text{NH}_2\text{COO}^- + \text{H}_2\text{O} \xrightarrow{k_{-8}} \text{NH}_3 + \text{HCO}_3^-$	72(5)	2.8×10^9	70(5)	-72(2)		
$\text{NH}_3 + \text{CO}_2 \xrightarrow{k_9} \text{NH}_2\text{COOH}$	51(1)	4.2×10^{11}	49(1)	-31(3)	-59(8)	-152(26)
$\text{NH}_2\text{COOH} \xrightarrow{k_{-9}} \text{NH}_3 + \text{CO}_2$	63(2)	7.7×10^{12}	60(2)	-7(6)		

Example 2:

morpholine

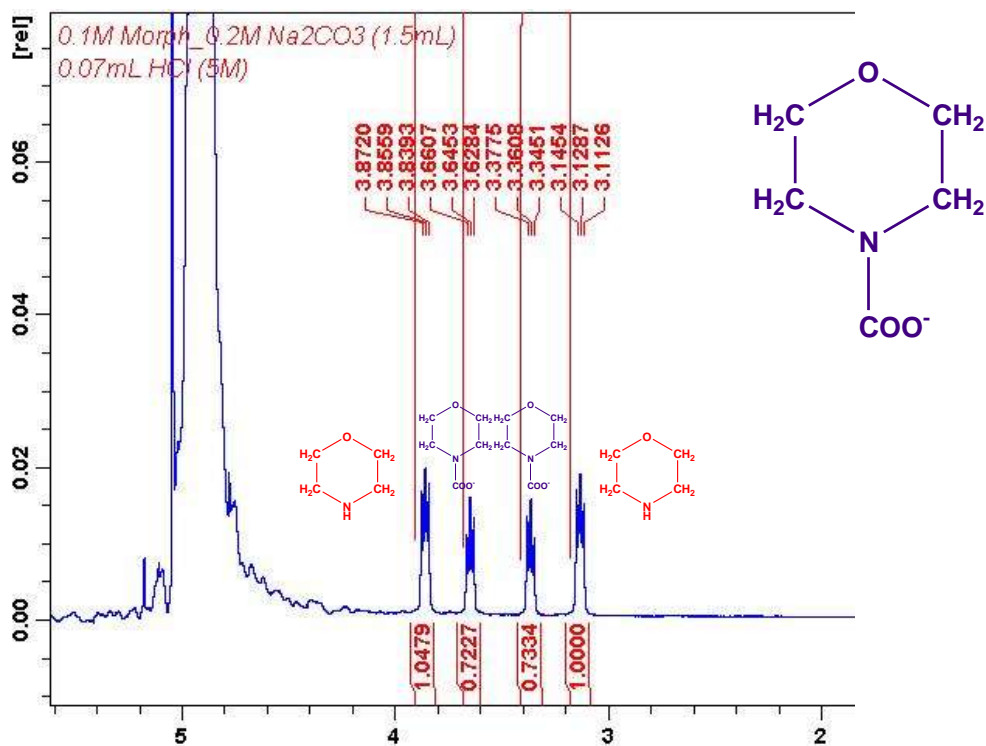


¹H-NMR spectra

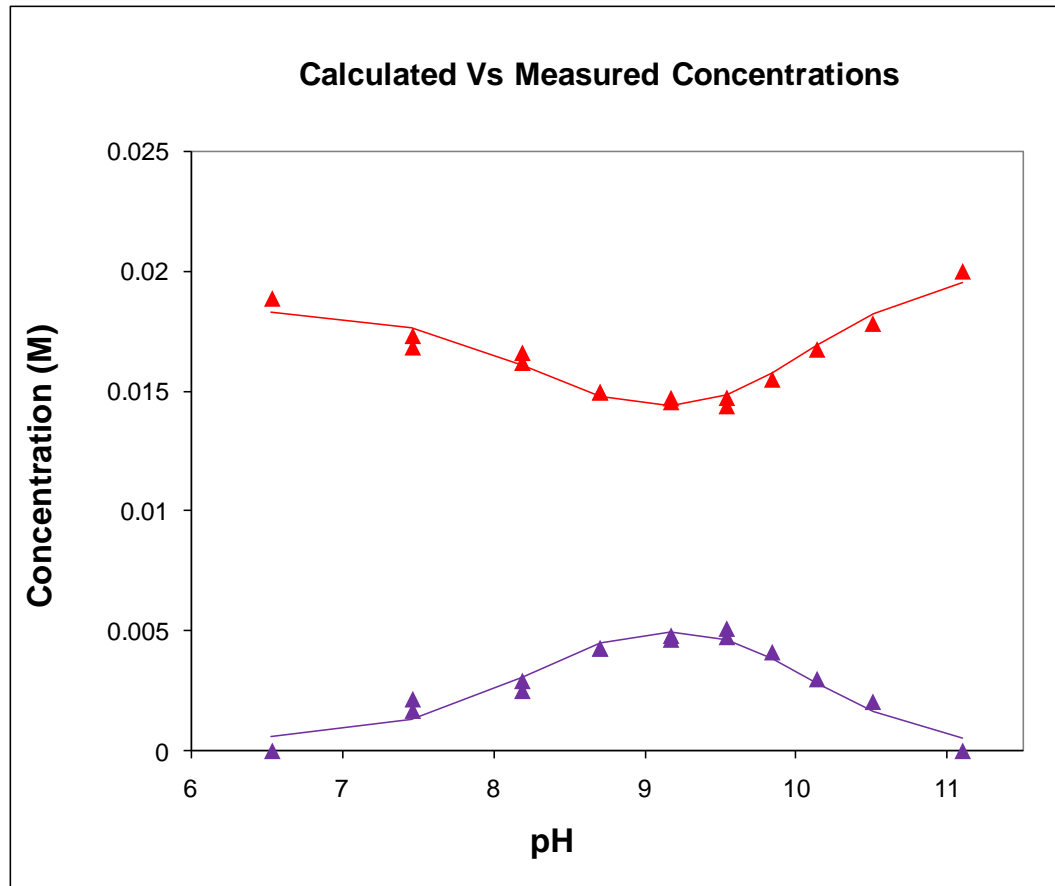


morpholine

morpholine
+
carbamate



Analysis of the data



Collaborations with

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 - Dr. Bob Burns
 - Dr. Raylene Dyson**
 - Dr. Nichola McCann**
 - Dr. Sarah Norman**
 - Dr. Xiaoguang Wang
 - Will Conway
 - Debra Fernandes
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 - Yaser Beyad
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 - Prof. Andreas Zuberbühler**
- **Institute for Chemical and Bioengineering, ETH Zürich, Switzerland**
 - Dr. Yorck-Michael Neuhold**
 - Prof. Konrad Hungerbühler
- **University of Kaiserslautern**
 - Prof. Hans Hasse
 - Dr. Nichola McCann**
- **CSIRO Energy Technology, Newcastle, Australia**
 - Dr. Graeme Puxty**
 - Dr. Paul Feron

Thank you for your attention

Positive proof of global warming.



1800's

1900's

1950

1970

1980

1990