Solvent Development for Aqueous Absorption/Stripping of CO_2

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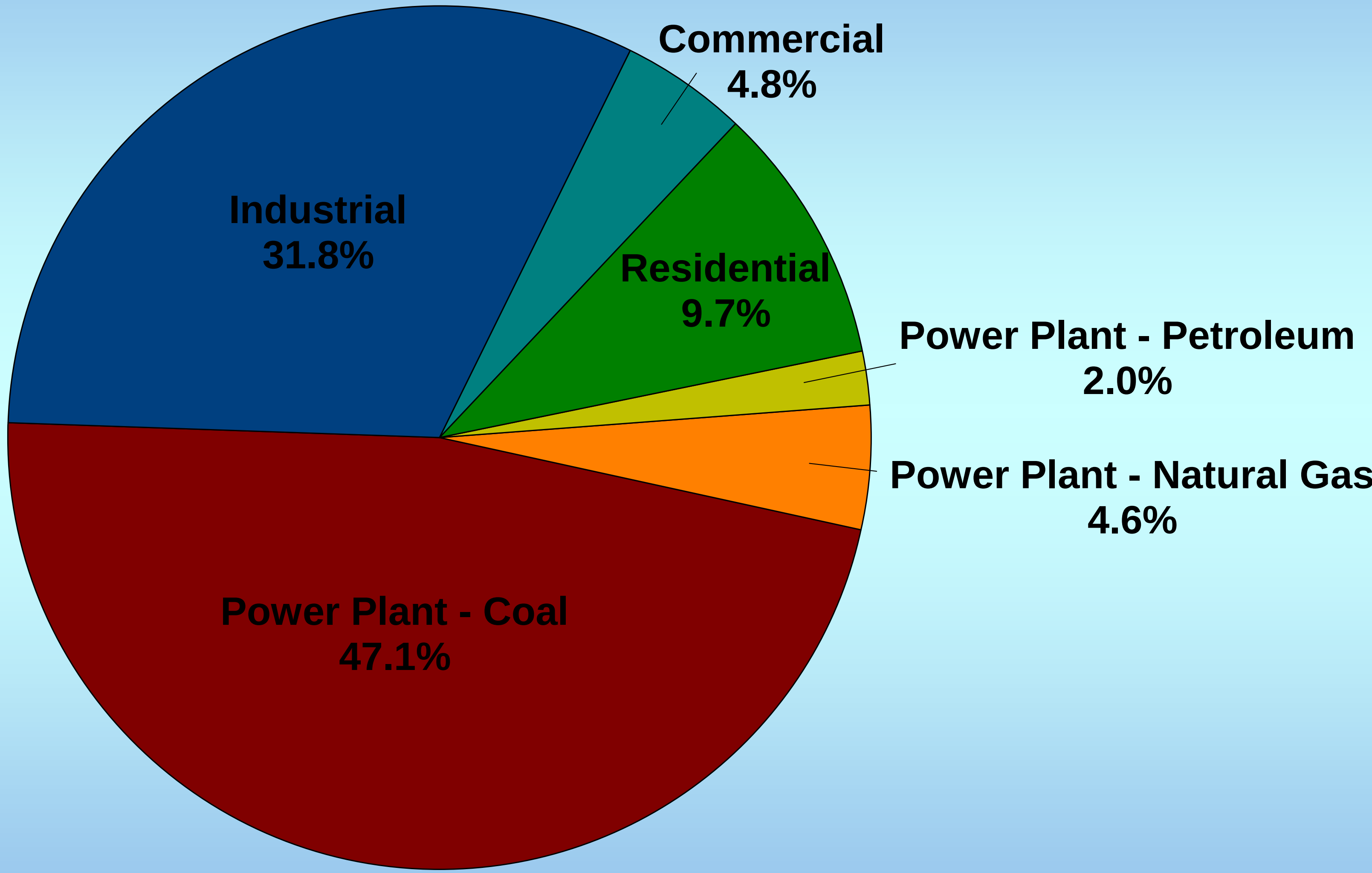
Outline

- Overview
- Process Considerations
- Solvent Development
  - Experimental Methods
  - Development of Aqueous K^+/PZ
- Other UT Research Activities
  - Degradation
  - Process Modeling
  - Pilot Plant/Packing Selection
- Conclusions

U.S. CO_2 Emissions from Fossil Fuel Combustion by Sector



Total U.S. Emissions = 3635.7 Tg CO_2 Eq.

Excludes Transportation, EPA (1999)

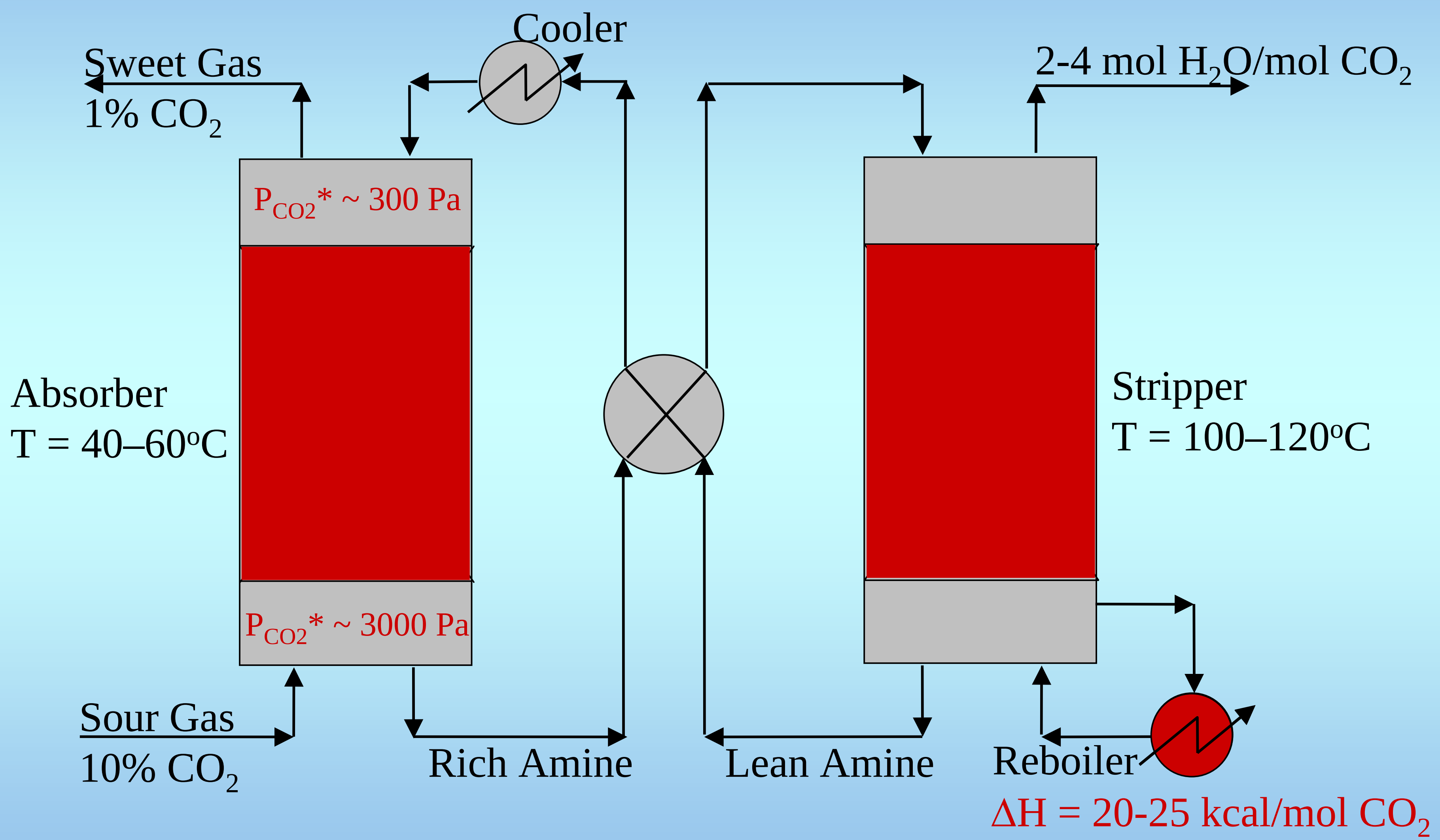
Advantages of Aqueous Absorption/Stripping

- Near Commercial Technology
  - Process used for treating H_2 & natural gas
  - MEA demonstrated on small coal plants
  - Promoted K_2CO_3 used for H_2 treating
- Post-process Technology Development
  - Lower cost and less risk to process
  - Resolve problems in small pilot plants
  - Demo Full-scale absorbers with 100 MW gas
- Problems
  - 20 - 40% energy use
  - High capital cost

Enhancing CO_2 Capture by Amines

1. Contactor Development
    - Packing
2. Process Flowsheet Innovations
    - Multi-pressure stripper
    - Inter-cooling
3. Energy Integration
    - Power plant specific
4. Engineering Development
    - Large-scale equipment
5. Solvent Development

CO_2 Capture by Amines



Solvent Development K^+/PZ

1. Thermodynamics
2. Rates of Absorption
3. Degradation

→ Bench-Scale Work

4. System Modeling

→ Fundamental

→ Process Flowsheet

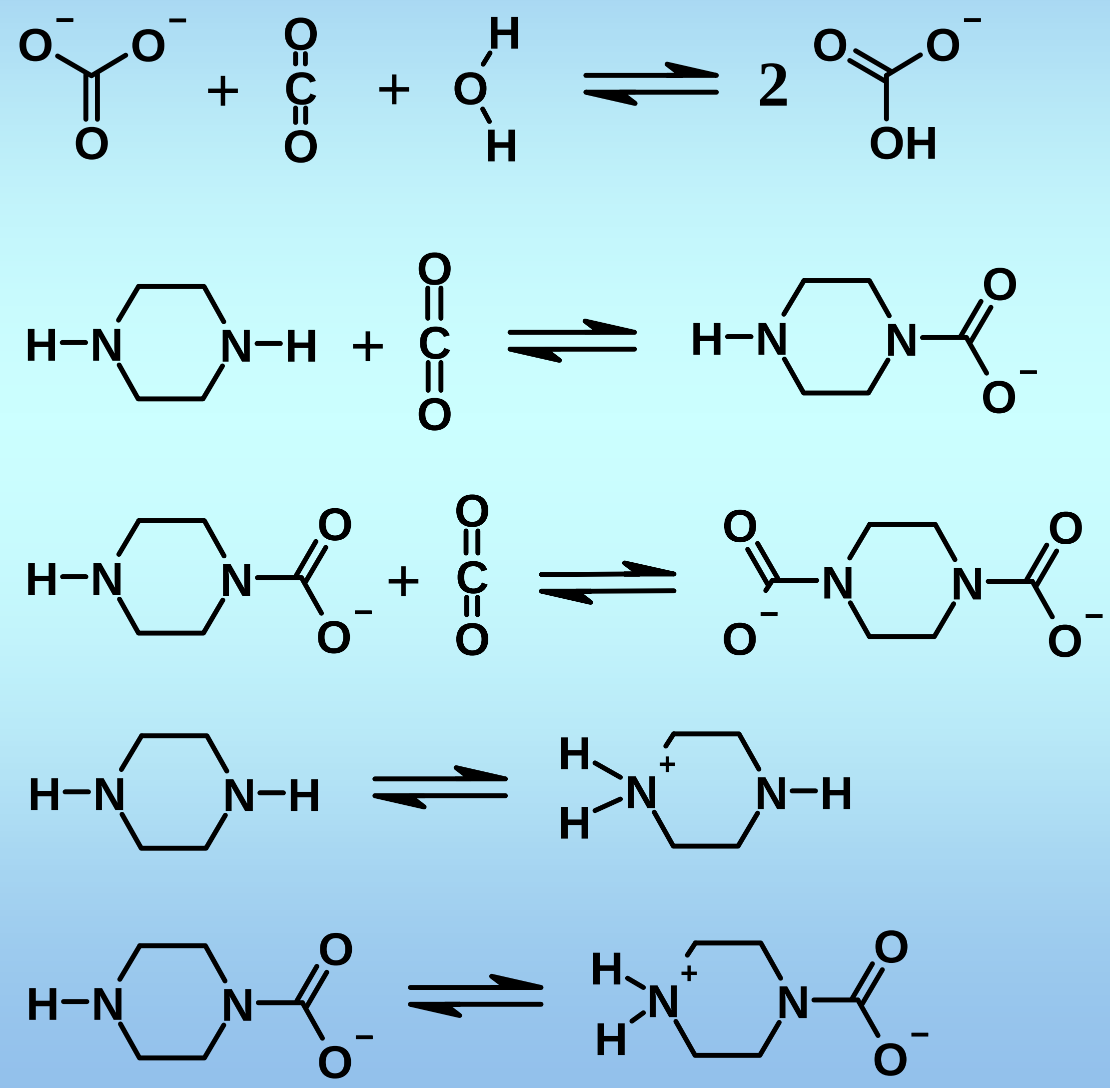
5. Pilot Plant

→ Large-Scale Work

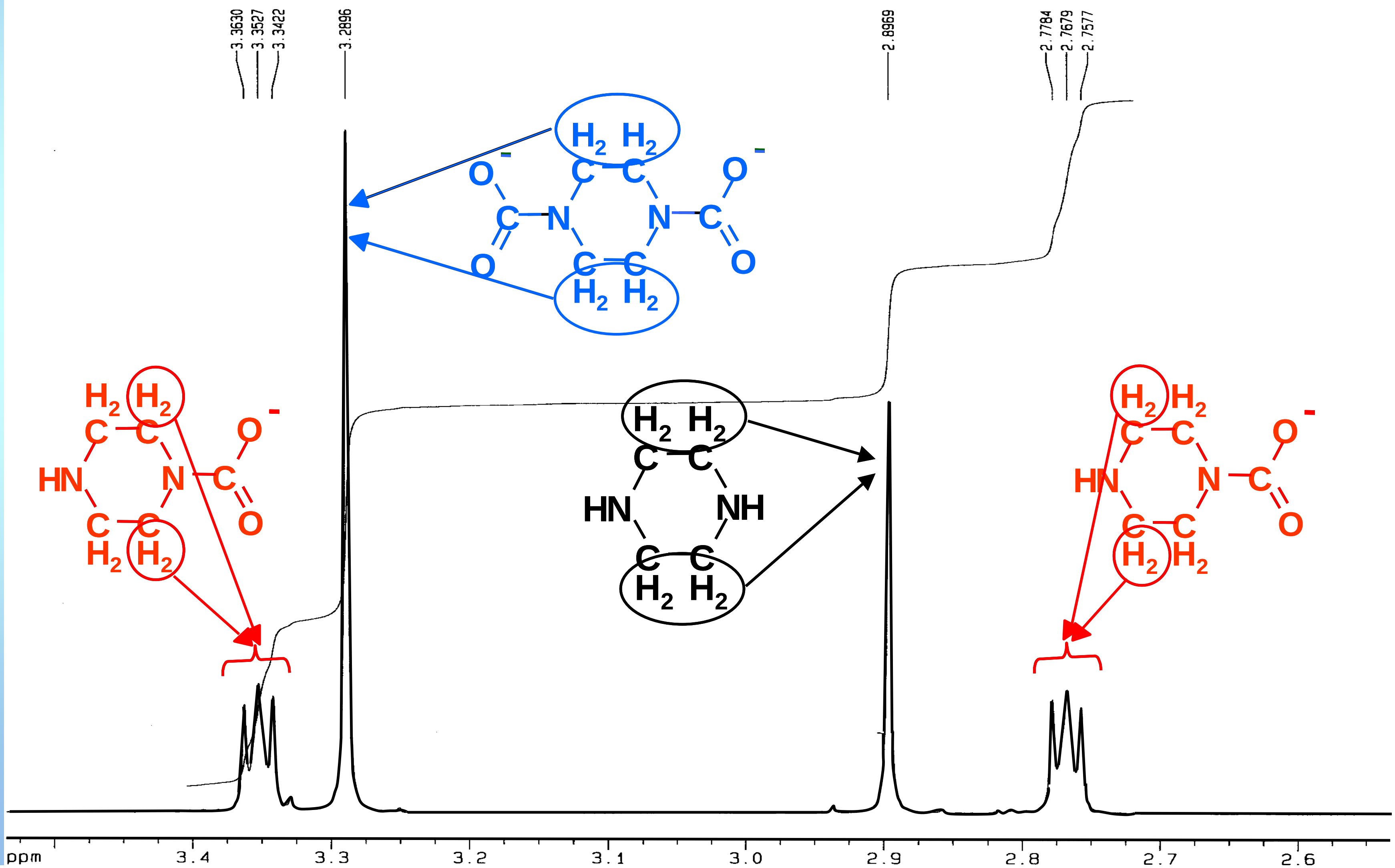
CO_2 Absorption by K^+/Piperazine

Carbonate Species

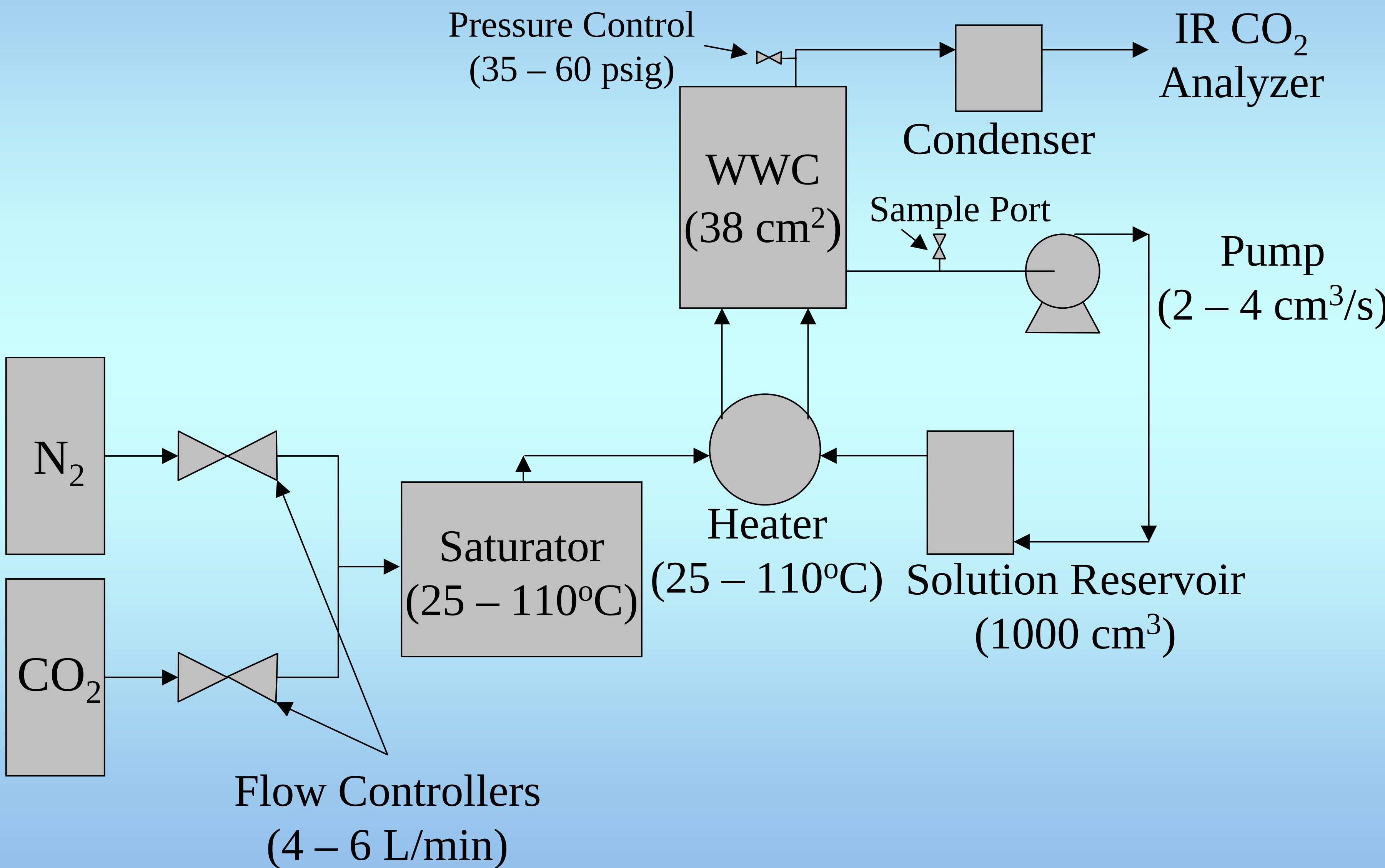
Piperazine Species



PZ Speciation by ^{1}H NMR



Wetted-Wall Column



Fundamental Equilibrium Modeling

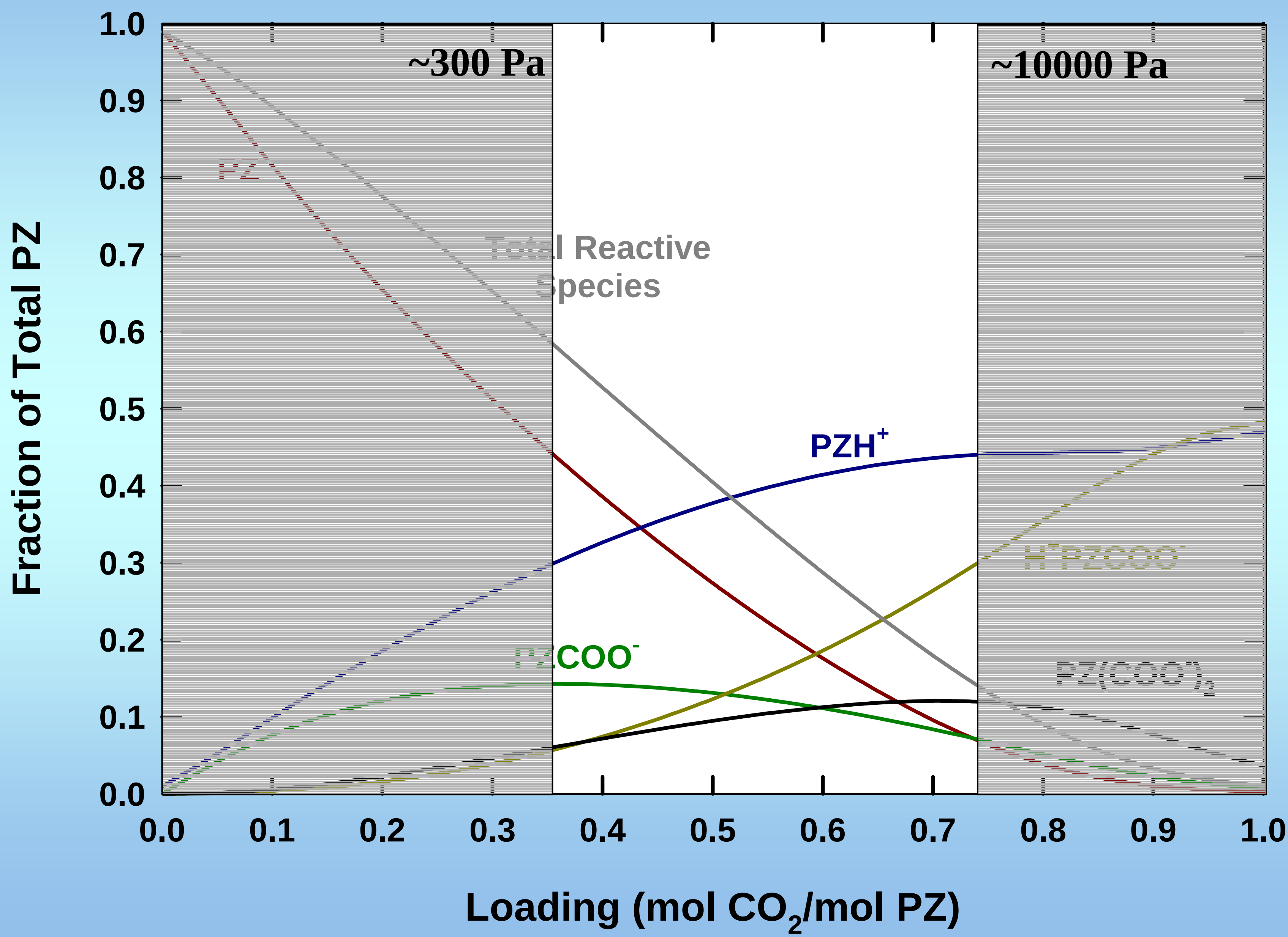
- Uses Electrolyte NRTL Model
  - Rigorous activity coefficient model
- Benefits
  - Versatile – can be used for broad range of conditions, systems
  - Develops/supported by theory – more accurate extrapolations
  - Predicts complicated behavior
- Challenges
  - Accurate representation of entire system
  - Meaningful results – can require a lot of data
  - Thermodynamic consistency

Model Parameter Summary

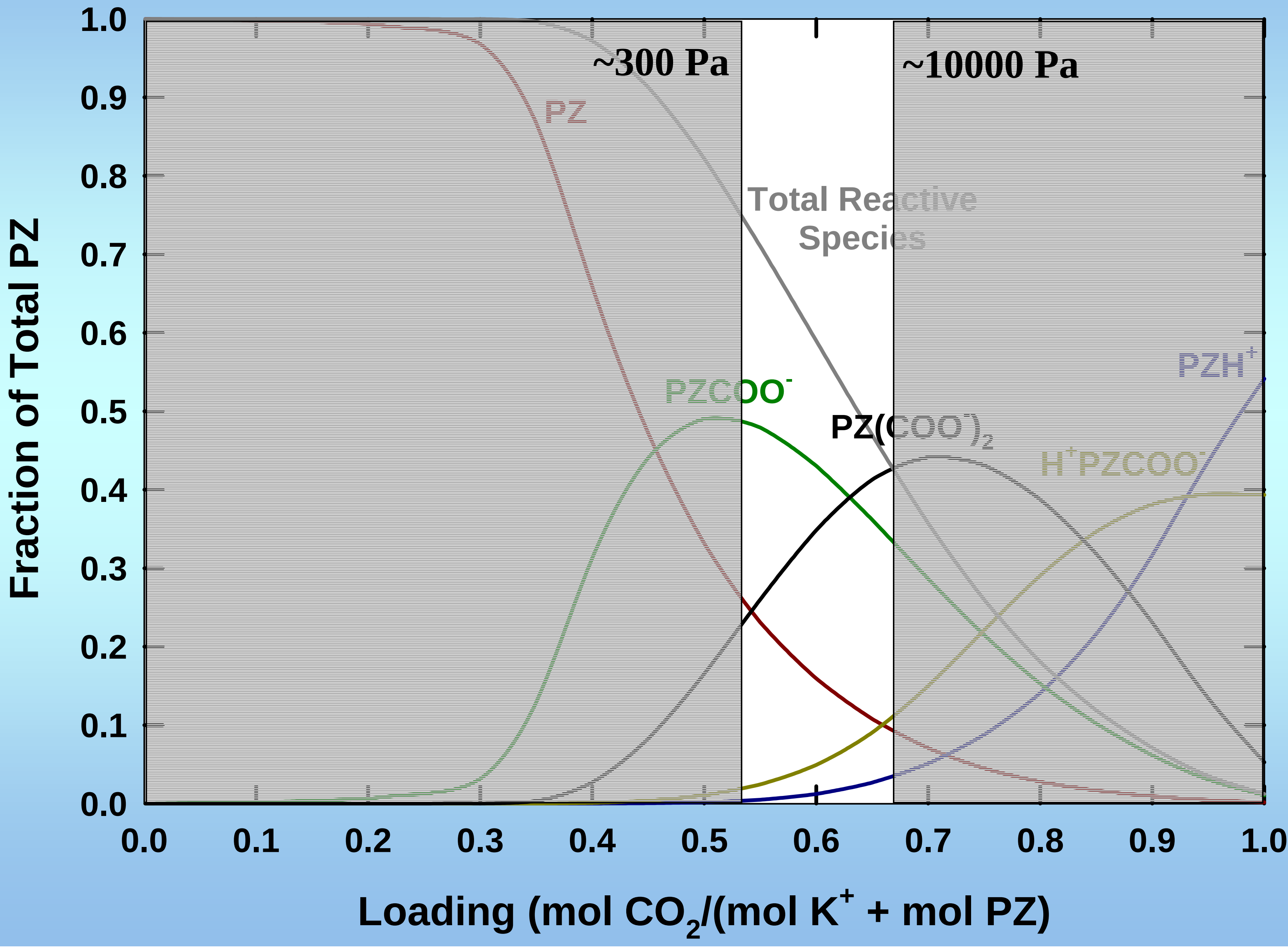
System	Data Types	Parameters	Data Points
K_2CO_3, H_2O	**Boiling pt. elev., P_{H2O}***	**4**	**681**
$KHCO_3$, K_2CO_3, H_2O	**P_{CO2}***	**4**	**120**
PZ, H_2O	**UNIFAC**	**4**	**21**
PZ, CO_2, H_2O	**NMR, P_{CO2}***	**3[a]**	**406**
PZ, K^+, CO_2, H_2O	**NMR, P_{CO2}***	**7**	**203**

a. 6 parameters for equilibrium constants also regressed

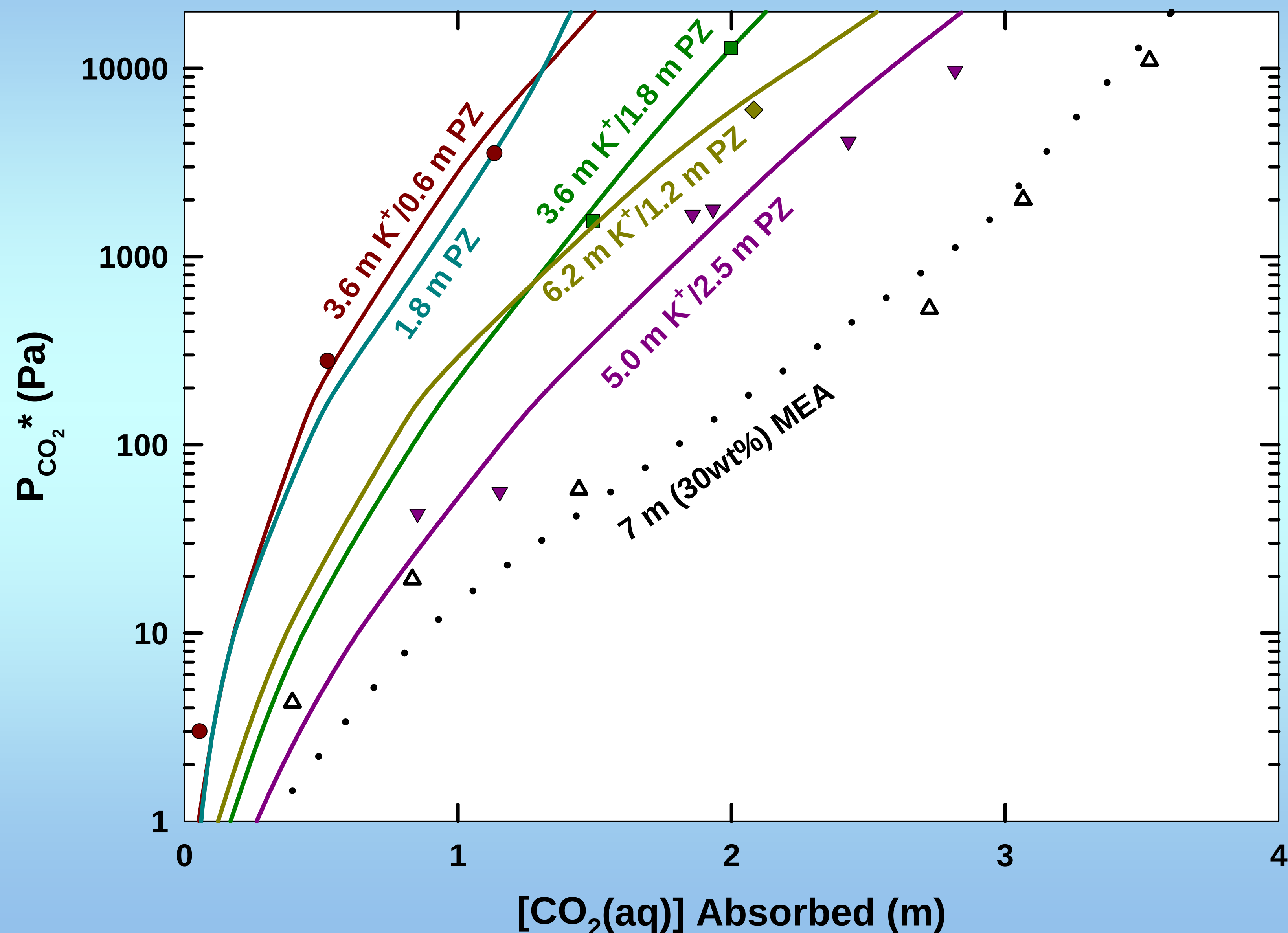
Speciation in 1.8 m PZ at 60°C



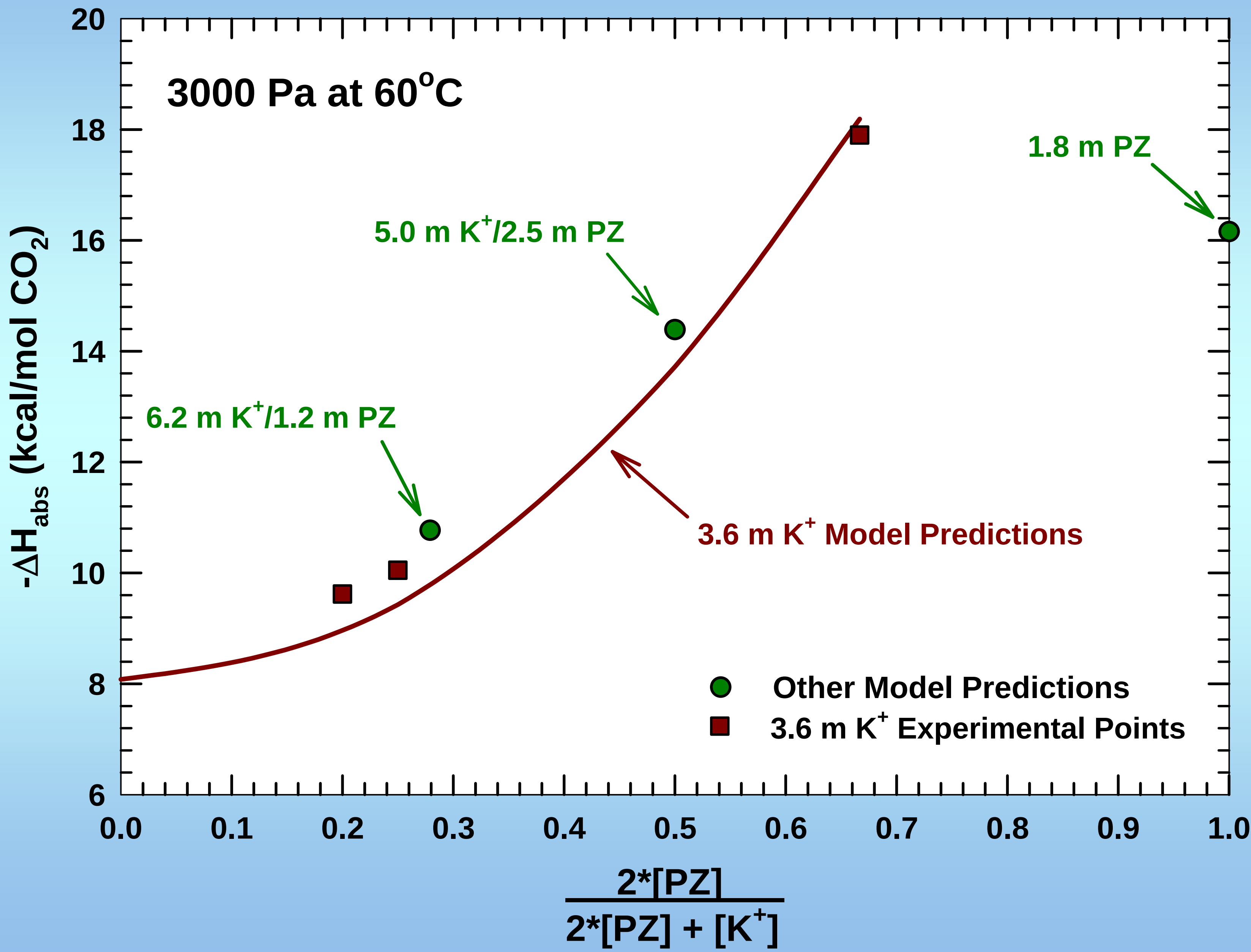
Speciation in 5.0 m K^+/2.5 m PZ at 60°C



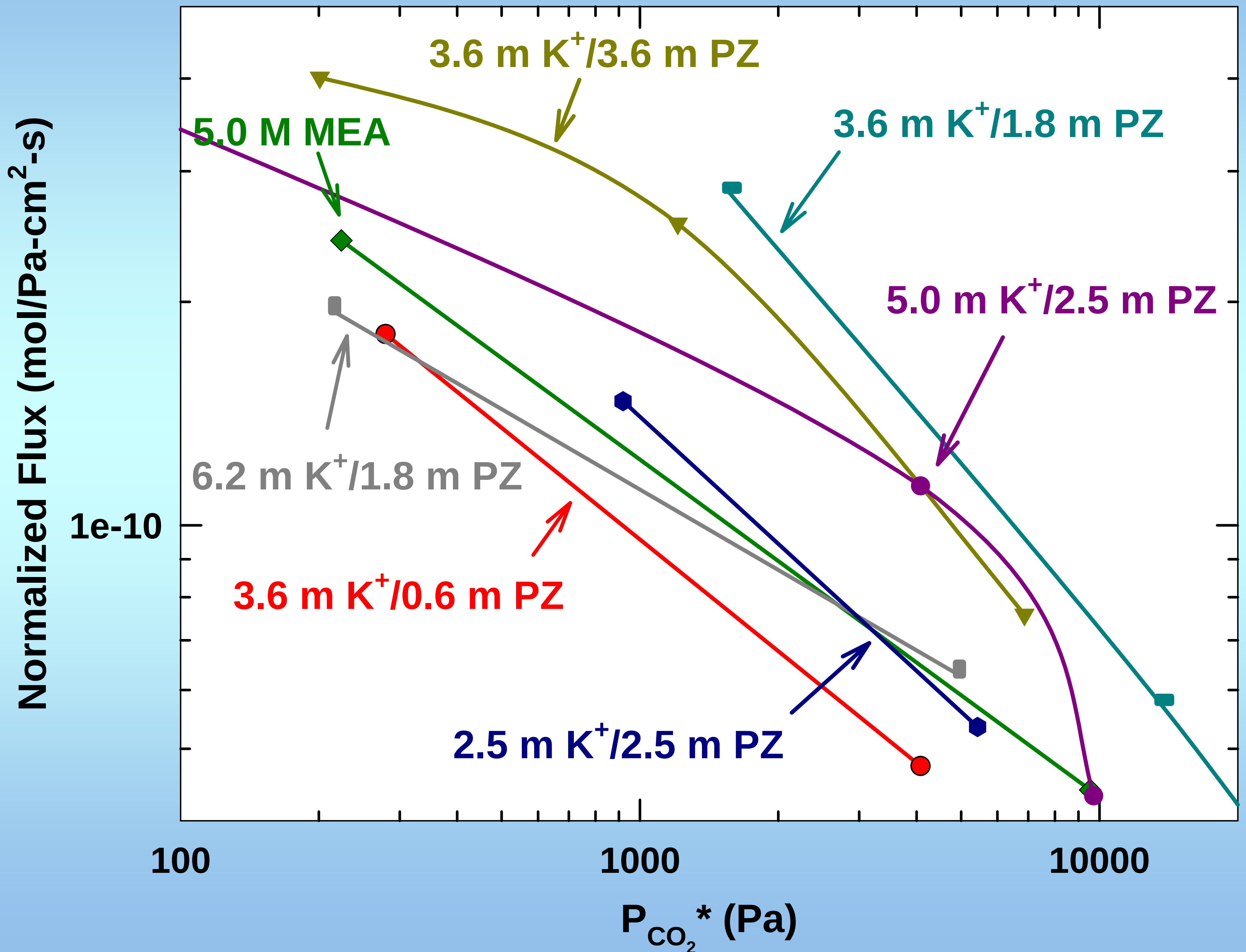
Equilibrium in K^+/PZ at 60°C



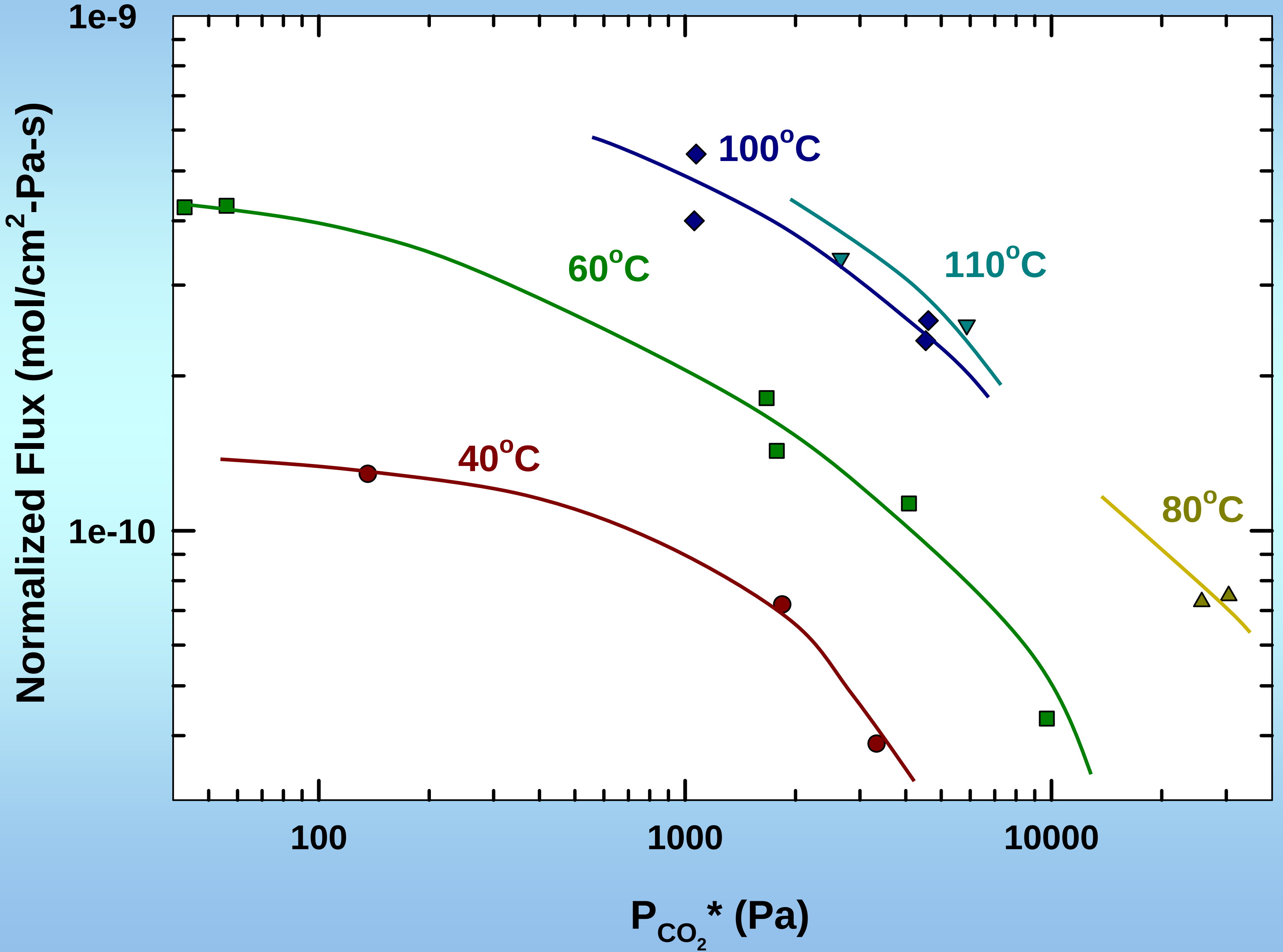
Heat of Absorption



Normalized Flux at 60ºC



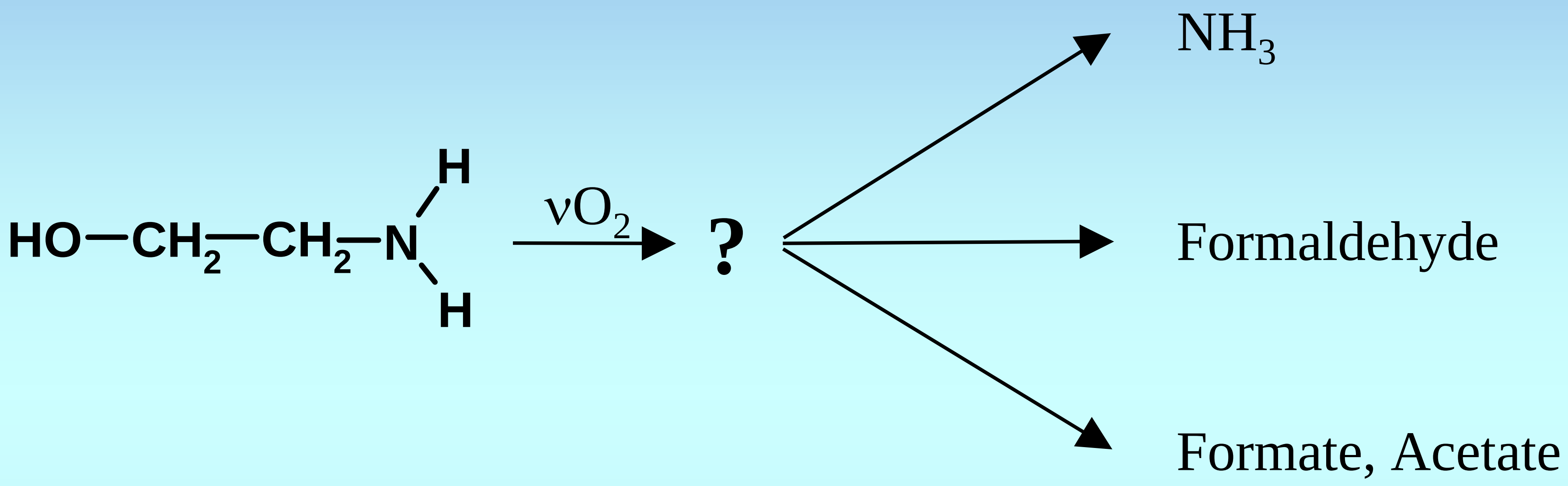
Absorption Rate in 5.0 m K^+/2.5 m PZ



Research Activities at UT

- Bench-scale
  - Wetted-wall Column – VLE, rates
  - NMR – speciation
  - Degradation
  - Other – solid solubility, transport properties
- Modeling
  - Thermodynamics
  - Rate
  - Process
- Pilot Plant
  - Contactor Testing
  - Solvent Testing

Oxidative Degradation of MEA



- Rate is measured by NH_3 evolution from a sparged reactor vessel
  - Gas analysis is quick/liquid analysis requires long experiments
  - Uncertainty in the stoichiometry of O_2 in the reaction

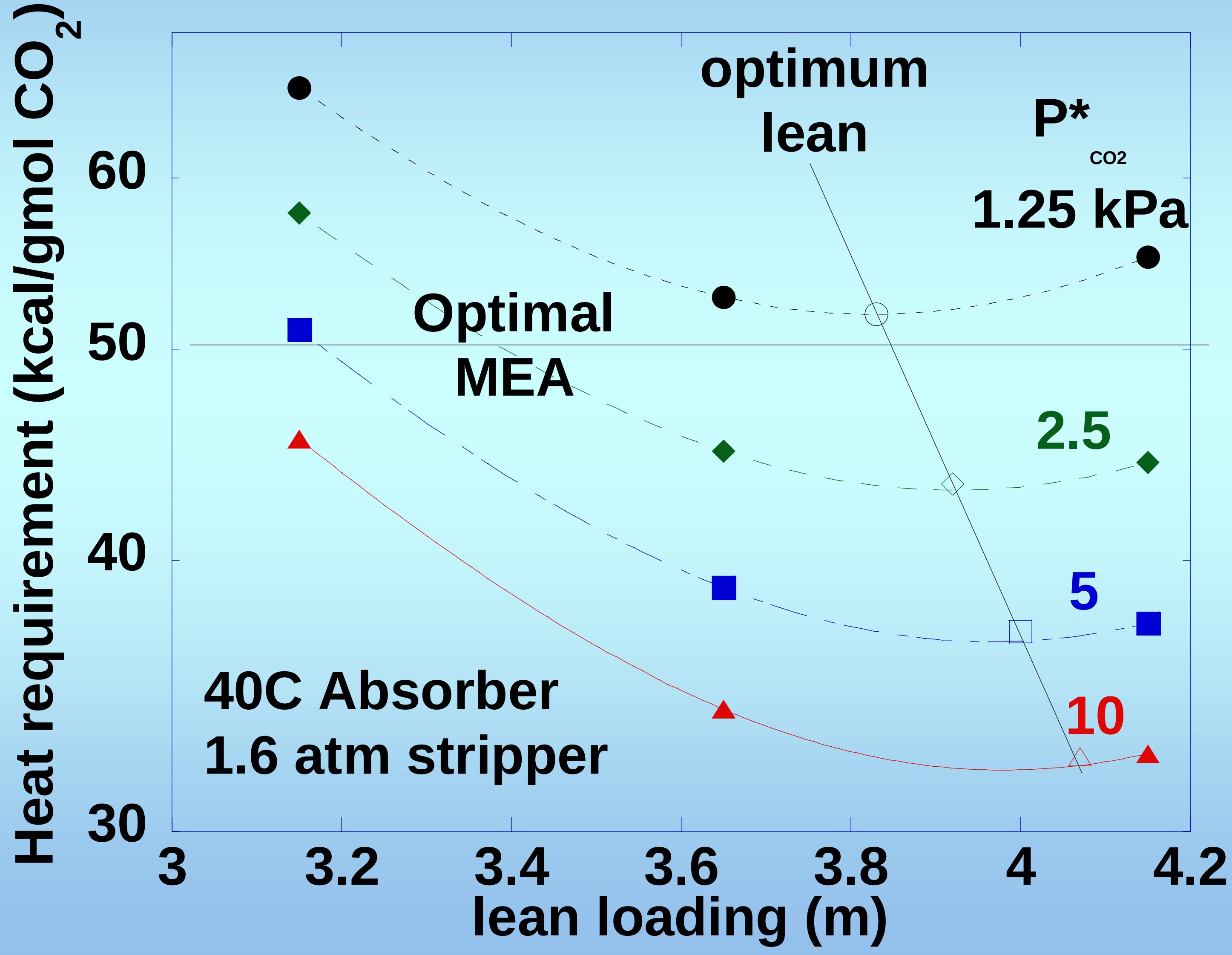
Degradation Results

Study	Sparge Gas	Gas Flow/Liq. Vol (min^{-1})	Max. Rate (mM/hr)
Rooney *et al.*	Air	0.006	0.4
Blachly and Ravner	Air	1.0	0.8
Girdler	50% O_2	1.0	2.6
Hofmeyer *et al.*	Pure O_2	2.9	5.0
Chi and Rochelle	Air	20.0	12.9
Goff and Rochelle	Air	25.0	27.8
	Air w/ Agitation	16.7	45.8

Conclusion: Mass Transfer Limited?

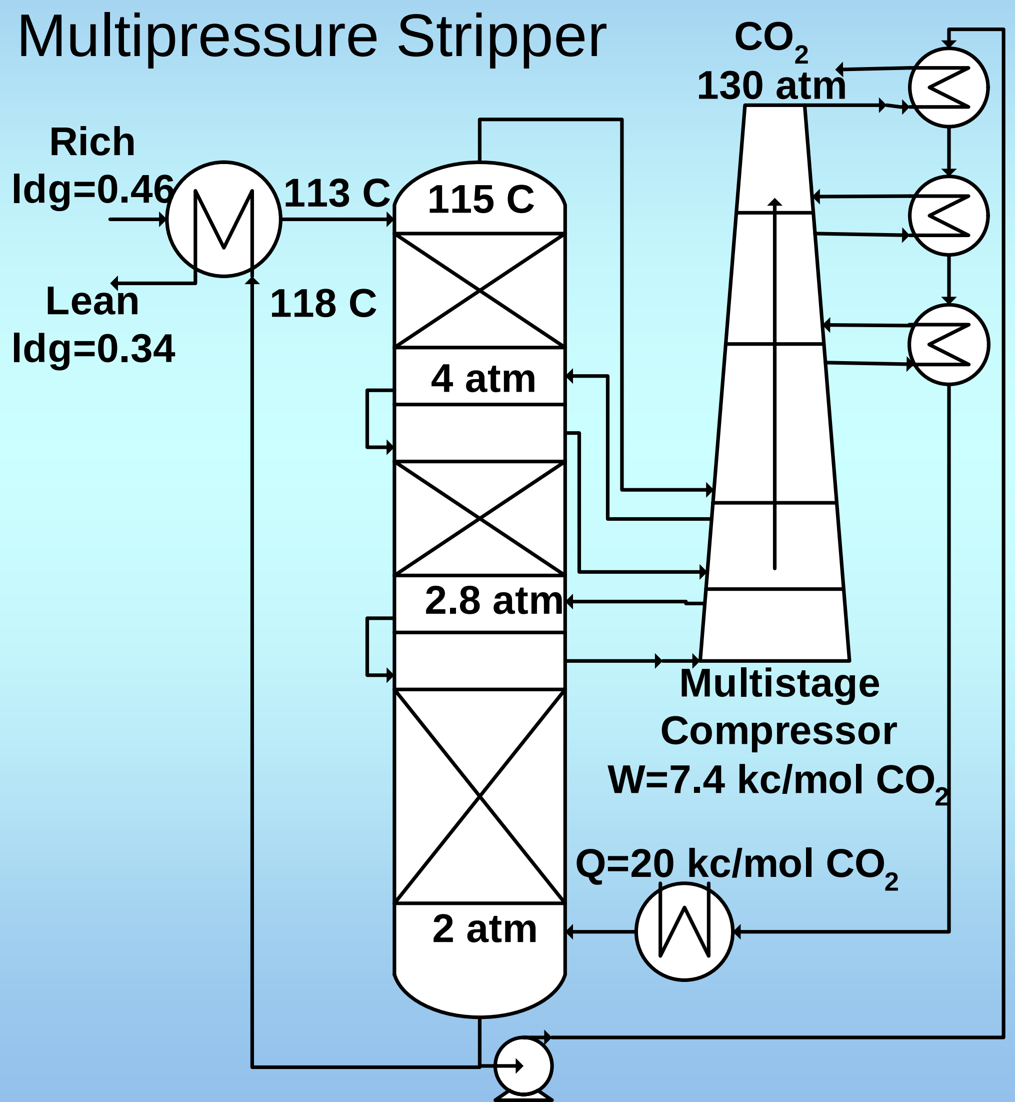
Process Modeling

- Explore Optimum Operating Conditions



Process Configuration

- Explore unique flowsheets



Pilot Plant at UT-SRP

- 18” PVC columns, 20 ft of packing
  - Accommodates commercial, structured packing
  - Operation as absorber or absorber/stripper
- Vacuum stripping
- Air/CO_2 Fed
  - Wide Range of Concentrations Possible

Pilot Plant Operation

- NaOH/Air – Screen packing areas
  - Packing areas based on 0.75” H_2O/ft, 5 gpm/ft^2

Packing	**Wetted Area (ft^2/ft^3)**
CMR 2”, plastic	27
IMTP #40	44
CMR 2”, metal	48
Montz B1-250	64
Montz B1-350	91

- Solvent – Simulation of absorber/stripper
  - Quantify “real” solvent performance
  - Includes impurities (Fe^{2+}, degradation, etc.)

Conclusions

- E-NRTL model describes speciation and VLE
- K^+ increases the amount of reactive species in solution
  - CO_3^{2-}/HCO_3^- is an effective buffer
  - Apparent carbamate stability is increased w/ K^+
- Solvent capacity increases with concentration and is comparable to MEA
- ΔH_{abs} can be lower than other amine-based systems and depends on the ratio of K^+:PZ
- Absorption rate is 1.5 to 4 times faster than MEA or other amine-promoted K_2CO_3 solutions

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Questions?