

γ, X^{sat}

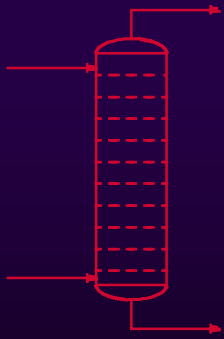
Measurement of Infinite Dilution Activity Coefficients and Miscibility Limits Using a Modified Total Pressure Method

Julie N. Howat & Colin S. Howat

Kurata Thermodynamics Laboratory

Department of Chemical & Petroleum Engineering

University of Kansas



γ, x^{sat}

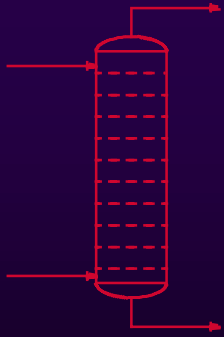
Measurement of Infinite Dilution Activity Coefficients and Miscibility Limits Using a Modified Total Pressure Method

Volatile Organic Chemical Phase Equilibria Research at KTL

Kurata Thermodynamics Laboratory

Department of Chemical & Petroleum Engineering

University of Kansas

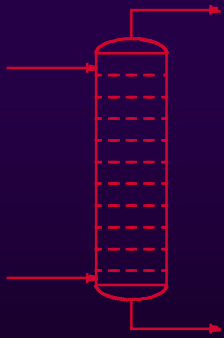


γ, X^{sat}

‘Stranger in a Strange Country.’

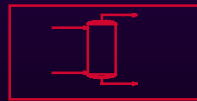
*Measurement of Infinite Dilution Phase Behavior
&
Miscibility Limits Using a Modified Total Pressure Method*

Kurata Thermodynamics Laboratory
Department of Chemical & Petroleum Engineering
University of Kansas



Outline

γ, x^{sat}



Motivation

VOC

Purpose



Experimental Equipment

S^2

Data Analysis

End Use

Experimental Design

γ, T

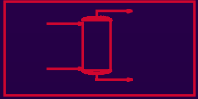
Experimental Data

γ, x^{sat}, T

Future Experimental Work

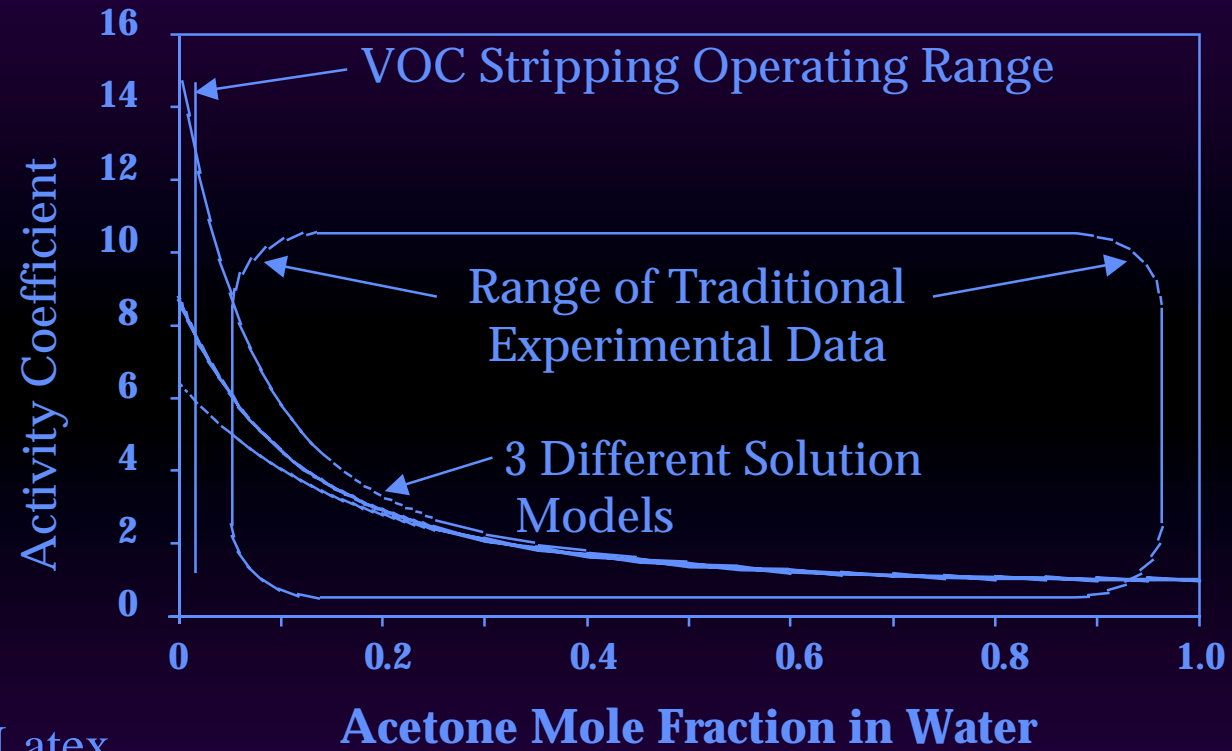
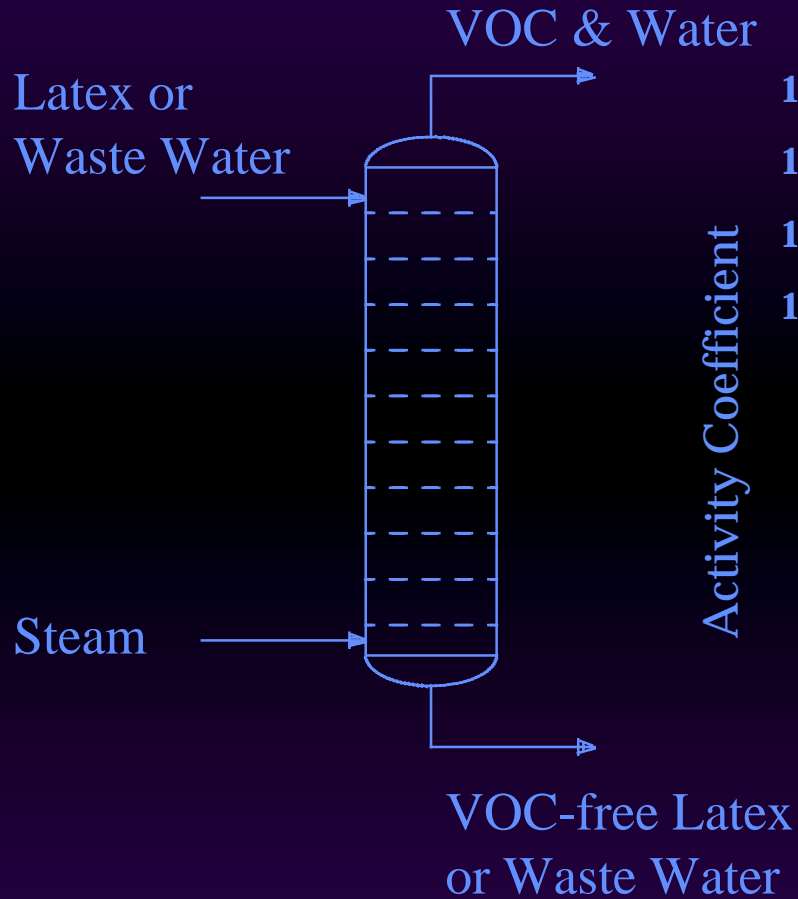
End

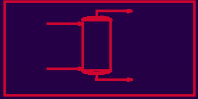
Conclusions



Motivation

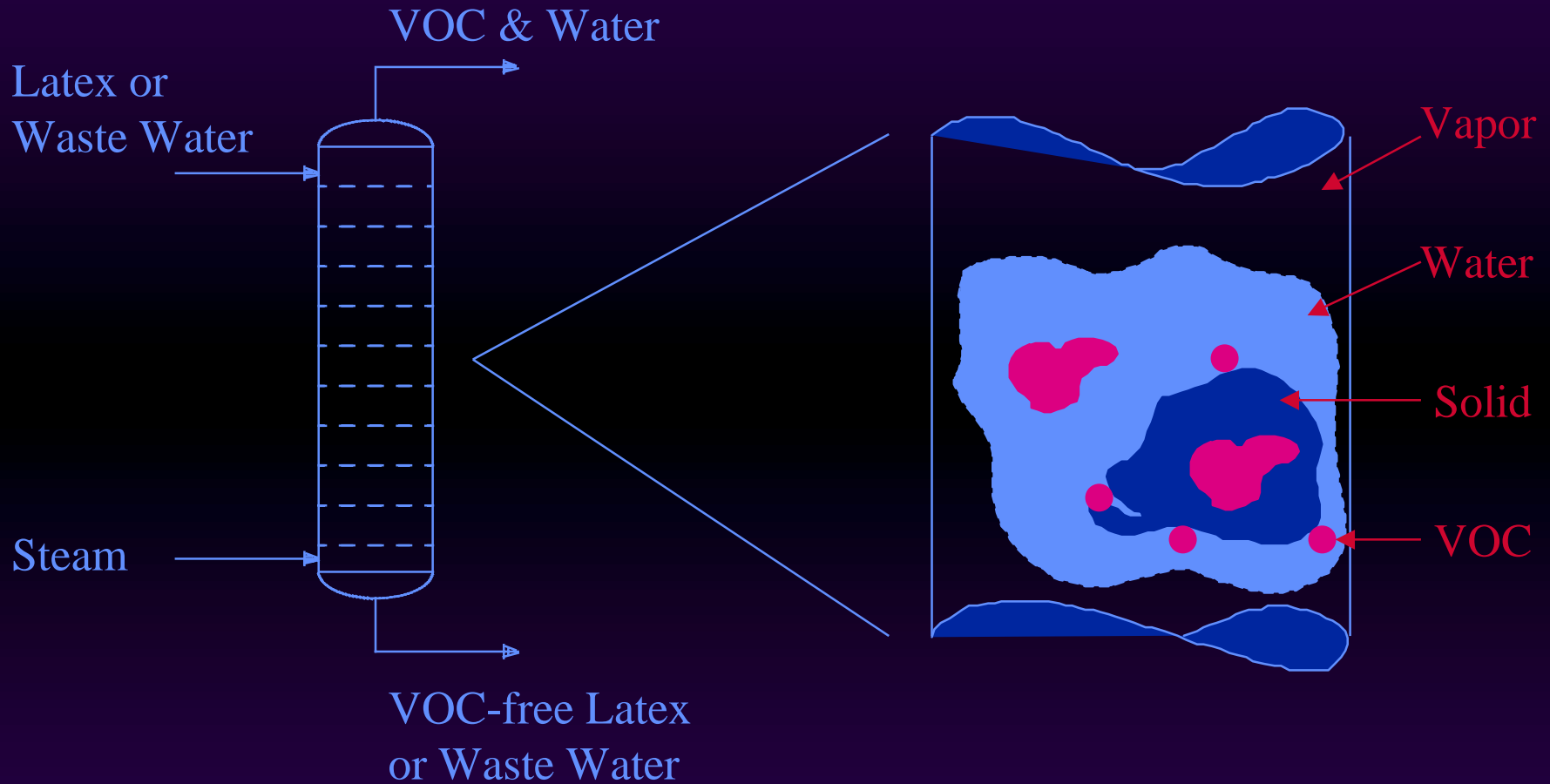
Uncertain VLE --





Motivation

To Complicate Matters Further --



Purpose

Purpose of this Project

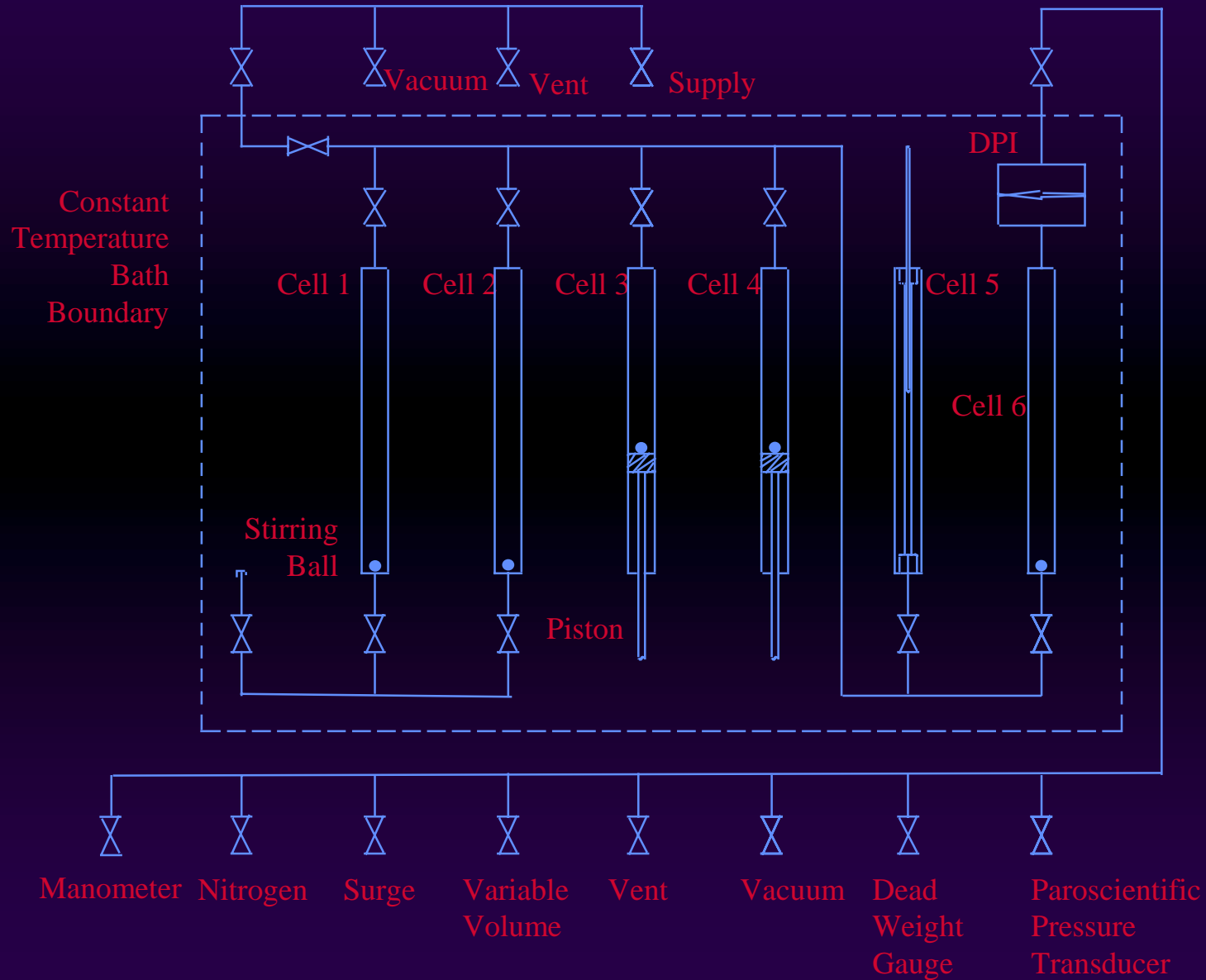
Experimental Determination of VOC - Water Systems exhibiting Limited Miscibility

Purpose of this Paper

Discussion of Data Analysis Method and Additional Base Experimental Data



Experimental Equipment



Data Analysis

By equating fugacities, equilibrium for a binary is --

$$P = \gamma_1 x_1 \phi_1^\circ P_1^\circ P_{C_1} / \hat{\phi}_1 + \gamma_2 x_2 \phi_2^\circ P_2^\circ P_{C_2} / \hat{\phi}_2$$

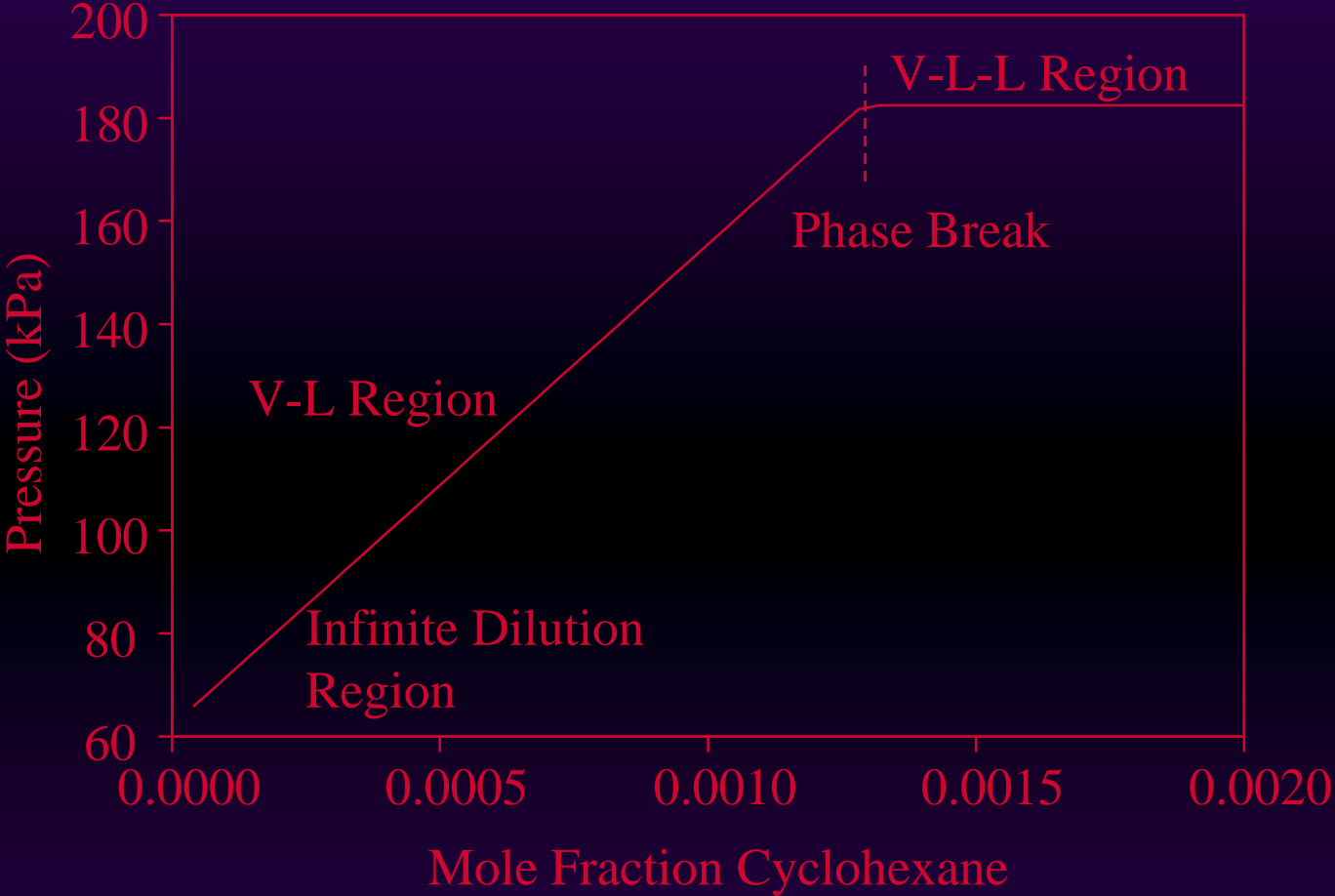
Rearranging and taking the limit as $x_1 \longrightarrow 0$

$$\gamma_1^\infty = (\hat{\phi}_1 P_2^\circ / \phi_1^\circ P_1^\circ) \left[1 + (\partial P / \partial x_1)_{x_1=0} \left((V_2^V - V_2^L) / RT \right) \right] \exp \int_{P_2^\circ}^{P_1^\circ} V_1^L / RT dP$$

Defining P_D as an excess pressure --

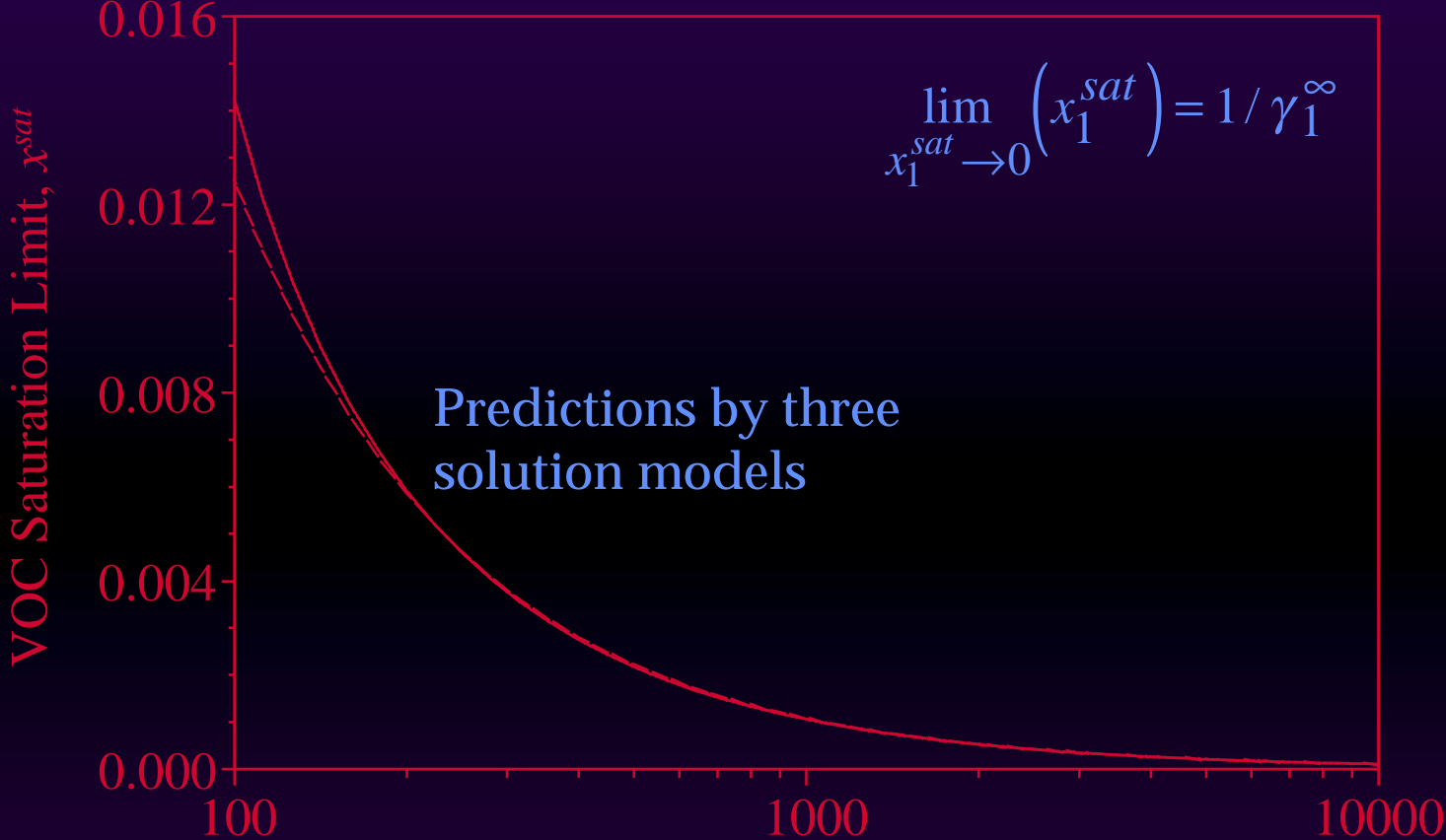
$$(\partial P / \partial x_1)_{x_1=0} = \lim_{x_1 \rightarrow 0} (P_D / x_1 x_2) - P_1^\circ + P_2^\circ$$

Data Analysis



Experimental regions defined by the experimental errors and system nonideality affect the accuracy and precision in the data and the data analysis procedures which can be used.

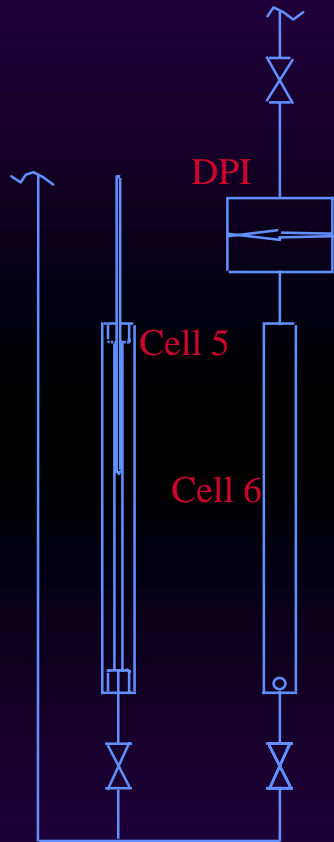
Data Analysis



Infinite Dilution Activity Coefficients ($\gamma_1^\infty = \gamma_2^\infty$)

The saturation limit is highly correlated with the activity coefficient which reduces bias caused by solution model.

Data Analysis



A large vapor space is maintained in Cell 6 to minimize effect of residual noncondensables.

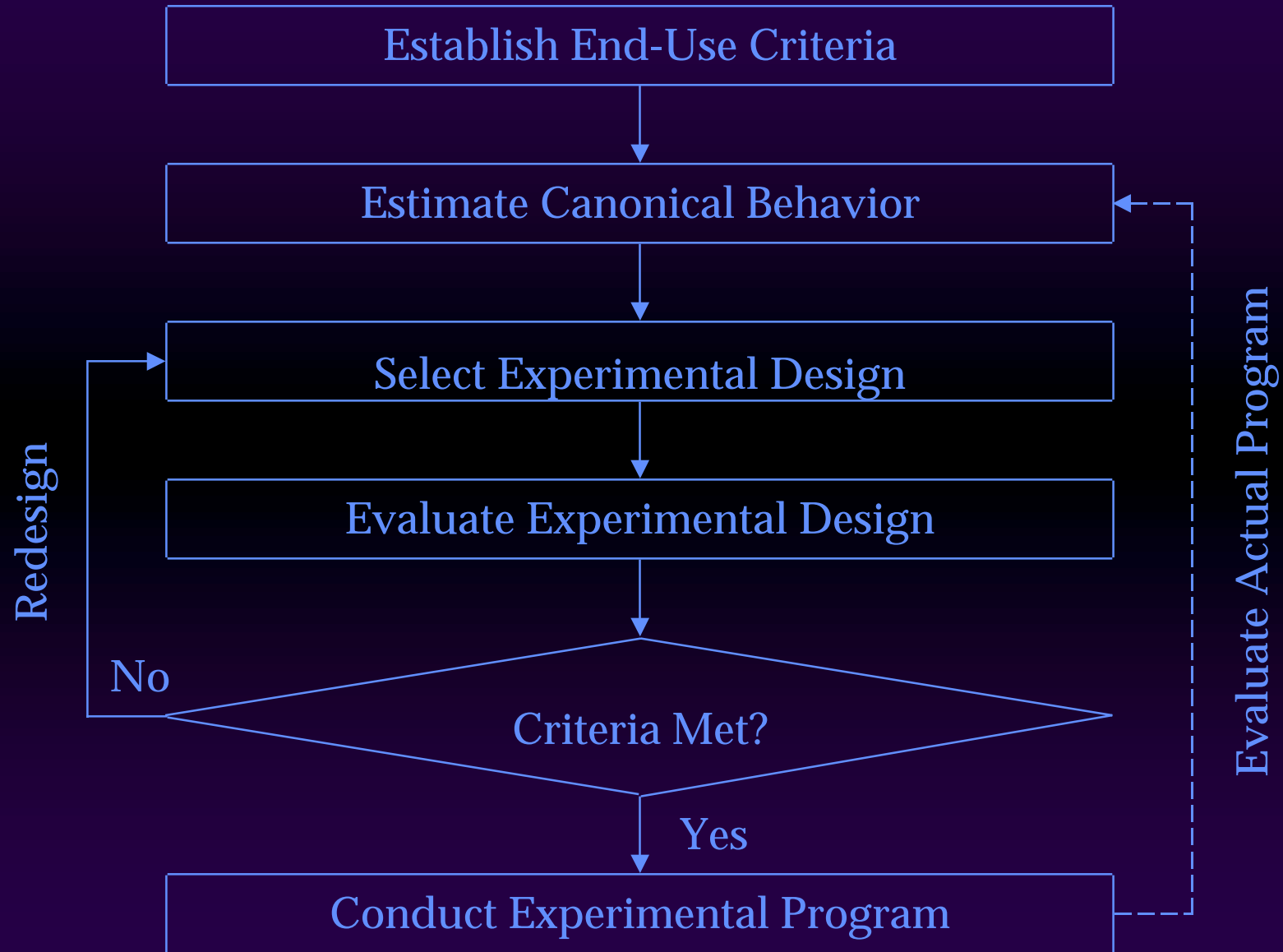
- *Bulk, not liquid, composition is known*
- *Flash required to estimate iteratively liquid composition*
- *Conventional flash calculation is over-specified*

∴ Experimental measurements lost in analysis -- unless

Plant performance analysis data reconciliation methods are incorporated into the analysis to adjust measurements (variables) and estimate compositions (parameters).

End Use

Experimental Design



Experimental Design

Questions Posed during the Experimental Design Analysis

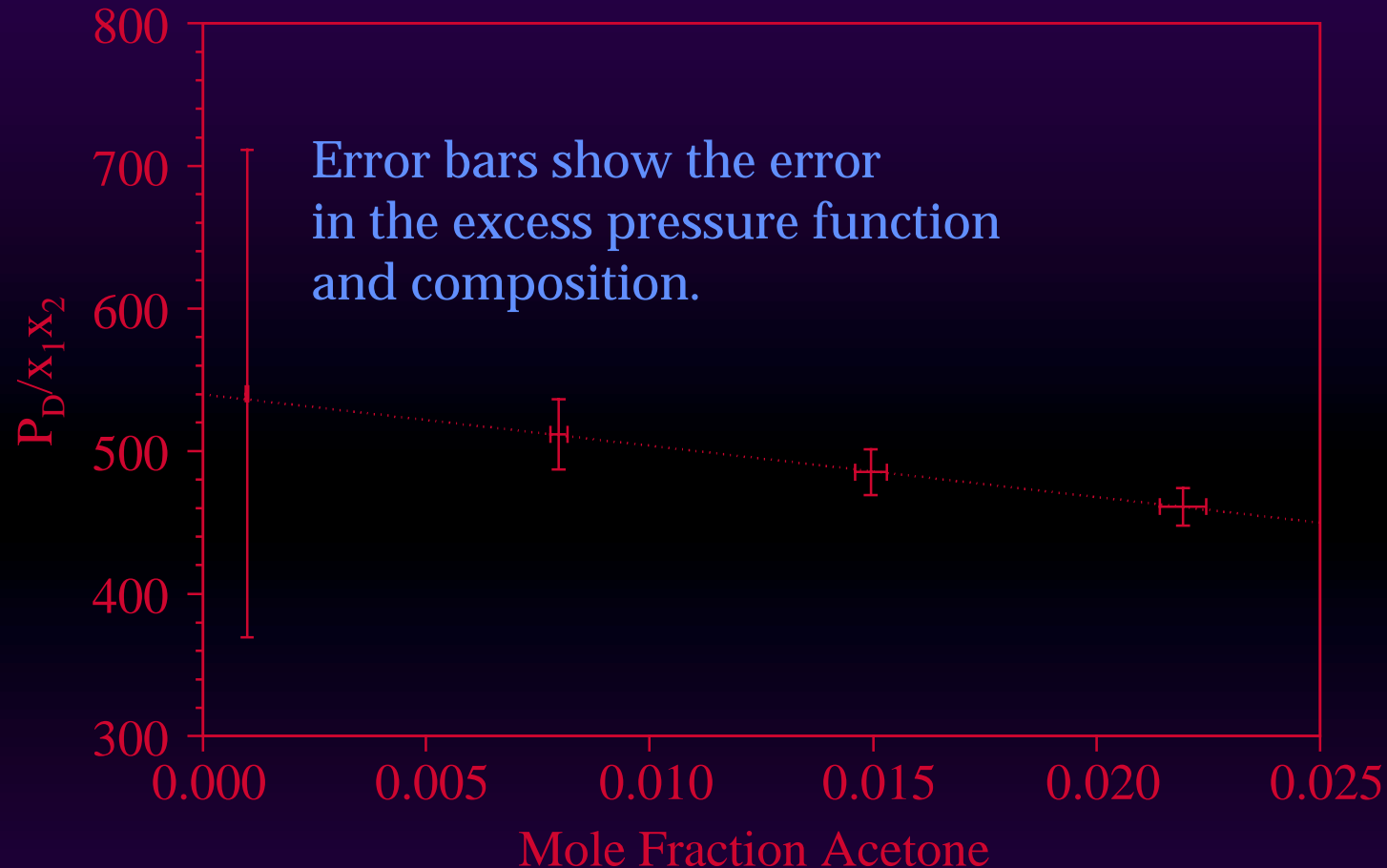
How do experimental errors impact upon γ ?

Does reconciliation improve the estimate in γ ?

Where is the Region 1 - 2 boundary?

Experimental Design

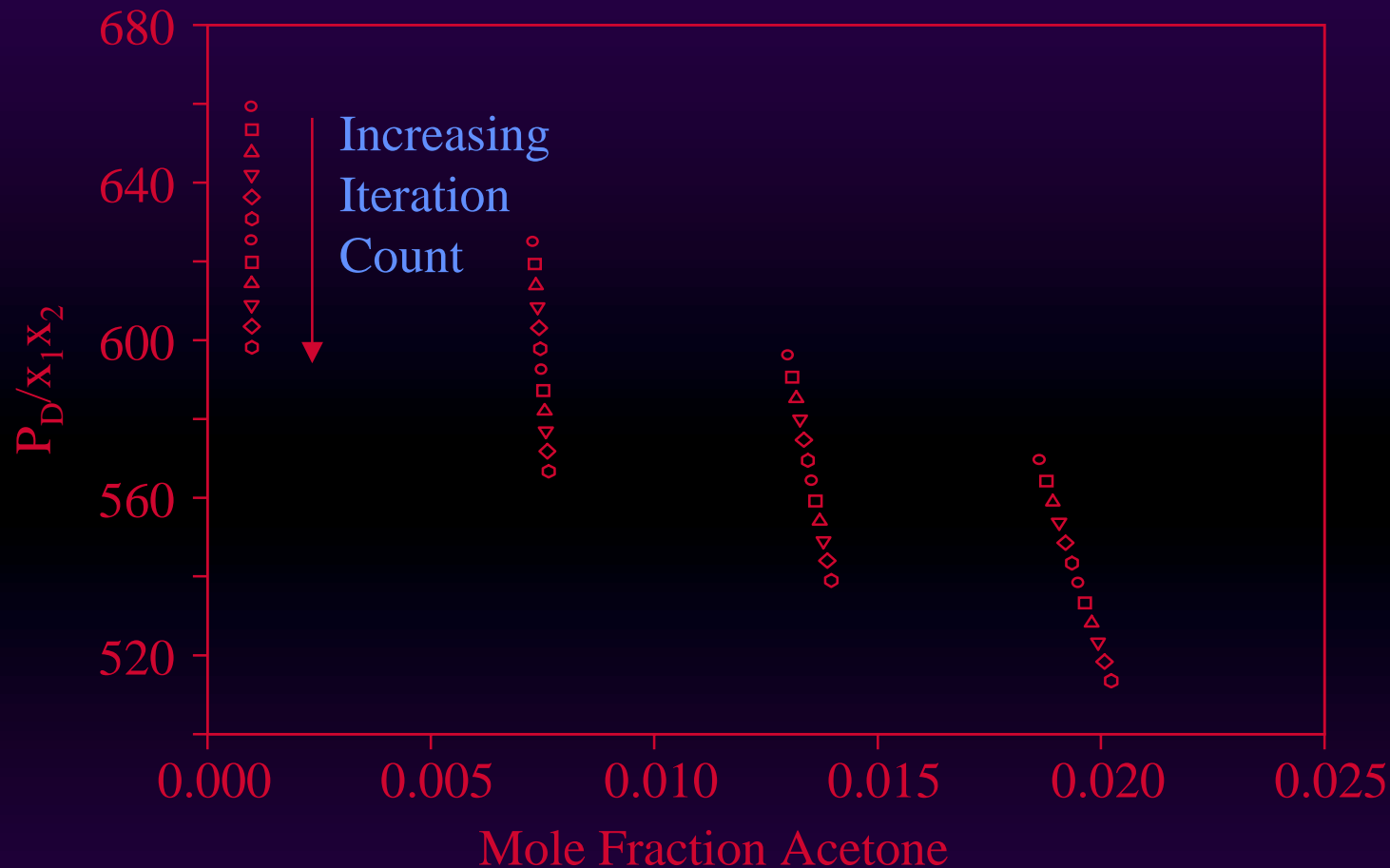
How do experimental errors impact upon γ ?



But, as the nonideality of the VOC - water system increases, the impact of composition error increases and ultimately dominates.

Experimental Design

Does reconciliation improve the estimate in γ ?



Use of all reconciled variables in the data analysis does not converge. Use of reconciled mole fractions results in marginal improvement.

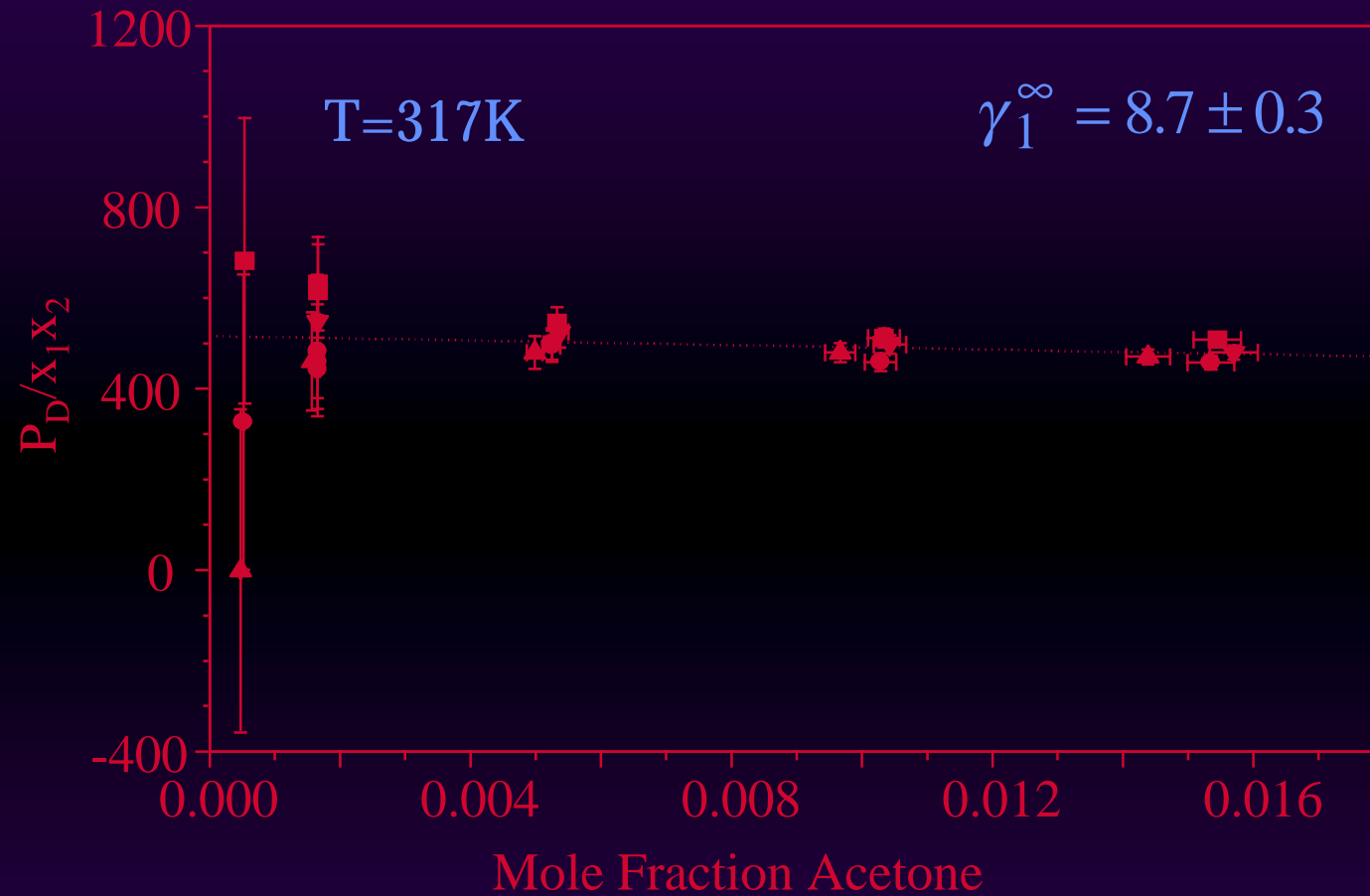
The composition - activity coefficient space was examined using typical experimental errors to determine boundary.

Canonical	Calculated	RSME
γ	γ	%
1000	990	6
2500	2350	20

Hydrocarbon VOC's similar to cyclohexane fall into Region 1 with the experimental equipment and errors used in this project.

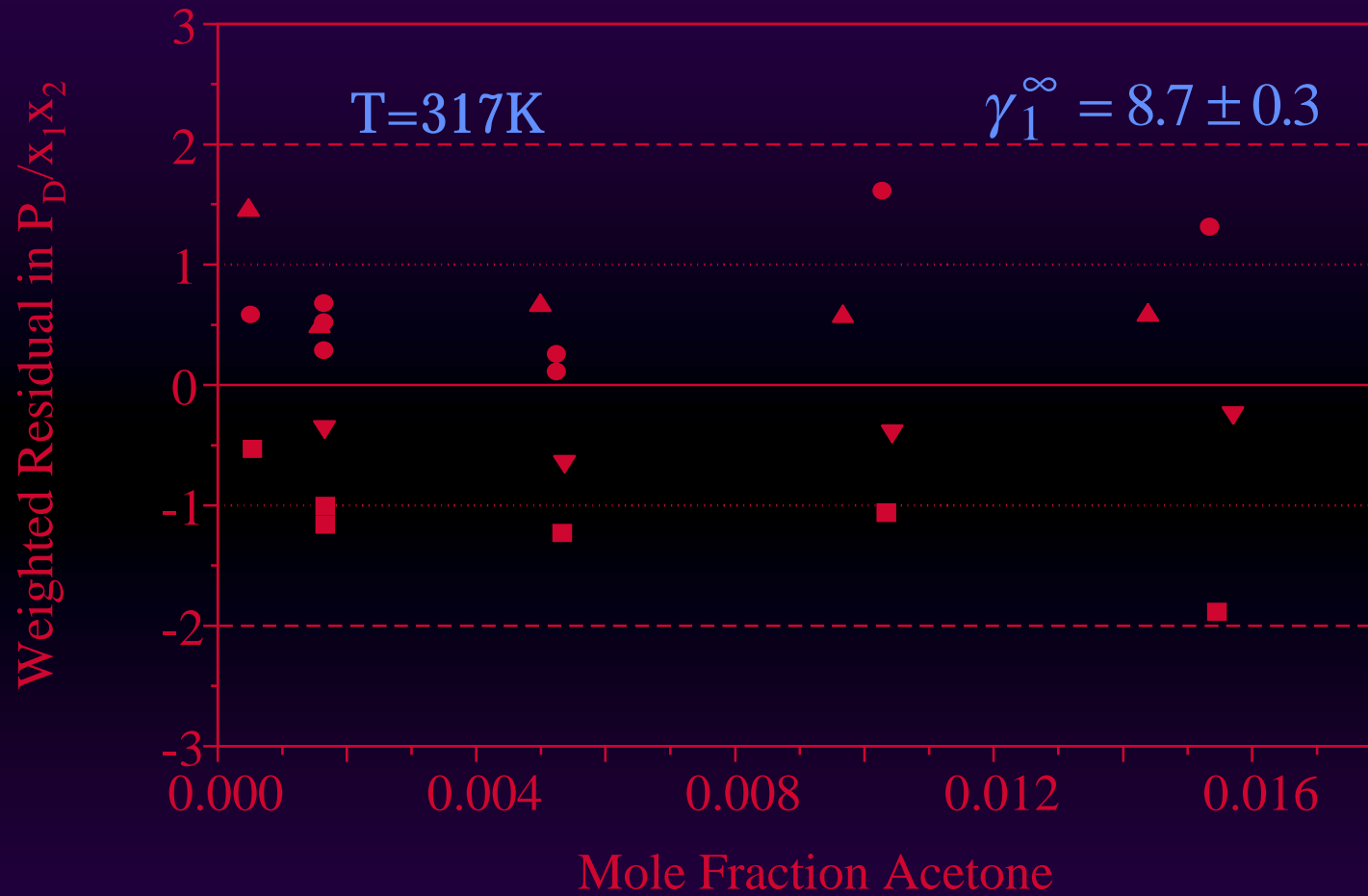
γ, T

Experimental Data



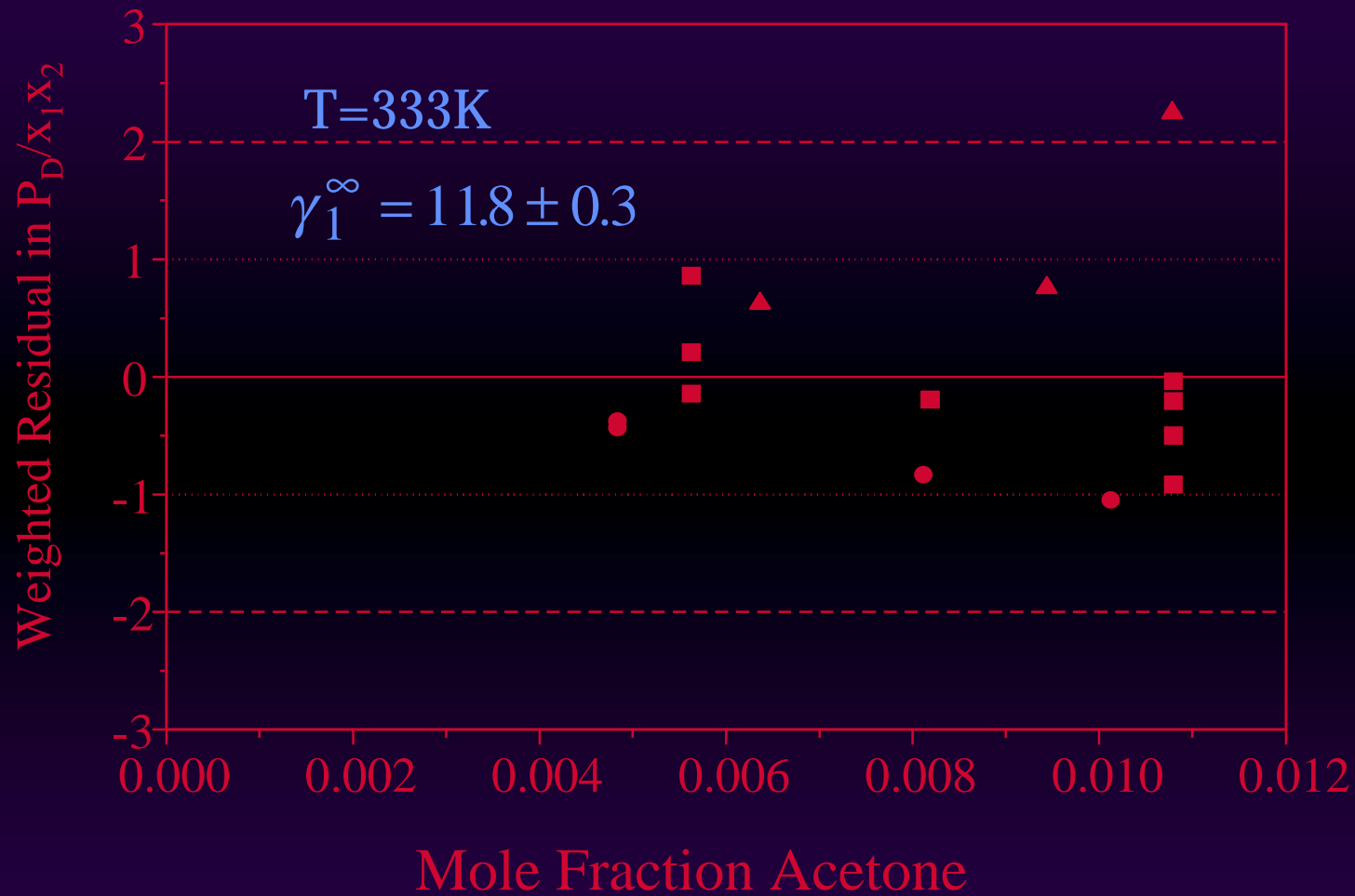
γ, T

Experimental Data



γ, T

Experimental Data



$$\gamma, x^{sat}, T$$

Future Experimental Work

Experimental Measurements:

- *Alcohols: n-Propanol, i-Propanol, n-Butanol*
- *Hydrocarbons: Pentane, Isoprene, Hexane, Cyclohexane*
- *Water in VOC's*

Future Experimental Work

Experimental Measurements:

- *VOC's in Water Environment*
n-Propanol, i-Propanol, n-Butanol
Pentane, Isoprene, Hexane, Cyclohexane
- *Water in VOC Environment*
n-Propanol, i-Propanol, n-Butanol
- *VOC's in Water/Solid/Latex Environment*

End

Conclusions

Relative Importance of Experimental Error Depends
Upon the Degree of Nonideality

Reconciliation is Sensitive to Bias in Pressure
Departure Function

Acetone - Water Data at 317K and 333K Reported

Equipment Reconfigured to Reduce Pressure Error
and its Impact on the Activity Coefficient

End

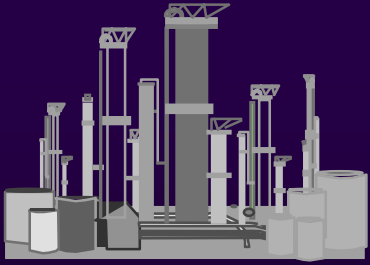
Conclusions

Impact of Experimental Errors Affects the Optimal
Experimental Design, Region Boundaries and
Uncertainty in the Results

Equipment Reconfigured to Reduce Pressure Error
and its Impact on the Activity Coefficient

Decoupled Reconciliation is Sensitive to Bias but
Coupled Method Shows Promise

Acetone - Water Data at 317K and 333K Reported



γ, X^{sat}

Overview of Research Activities at KTL

Improving Reliability, Reducing Risk & Accepting Uncertainty

C. S. 'Chip' Howat

Kurata Thermodynamics Laboratory

Department of Chemical & Petroleum Engineering

University of Kansas

