

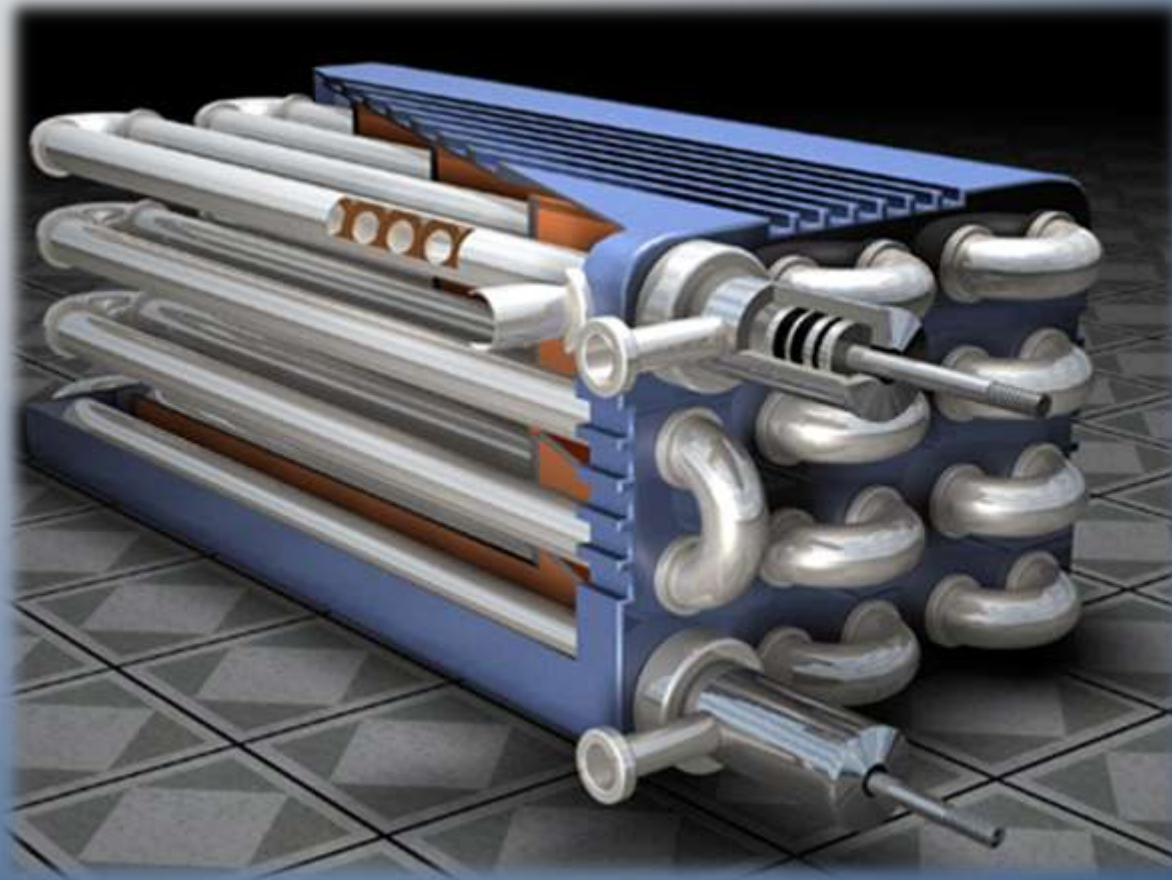
University of KwaZulu Natal Chemical Engineering

A New Group Contribution Method For The Estimation Of Thermal Conductivity For Non- Electrolyte Organic Compounds

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Experimentation Verses Prediction





Thermal Conductivity Required for

- ✱ Equipment design
- ✱ Cost-effective and safe plant design
- ✱ Simulation packages
- ✱ Scale up
- ✱ Calculation of transfer coefficients and dimensionless numbers





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- ✱ Equipment design
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Previous Work Done

- ✿ Normal boiling point (Rarey and Cordes 2002 and Nannoolal *et al.* 2004)
- ✿ Critical property data (Nannoolal *et al.* 2007)
- ✿ Vapour pressures (Nannoolal *et al.* 2008 and Moller *et al.* 2008)
- ✿ Liquid viscosity (Nannoolal *et al.* 2009)

Current Work

- ✿ Bruce Moller – Gamma infinity in water, alkanes, alcohols
- ✿ Eugene Olivier – Surface Tension
- ✿ Onellan Govender – Thermal Conductivity

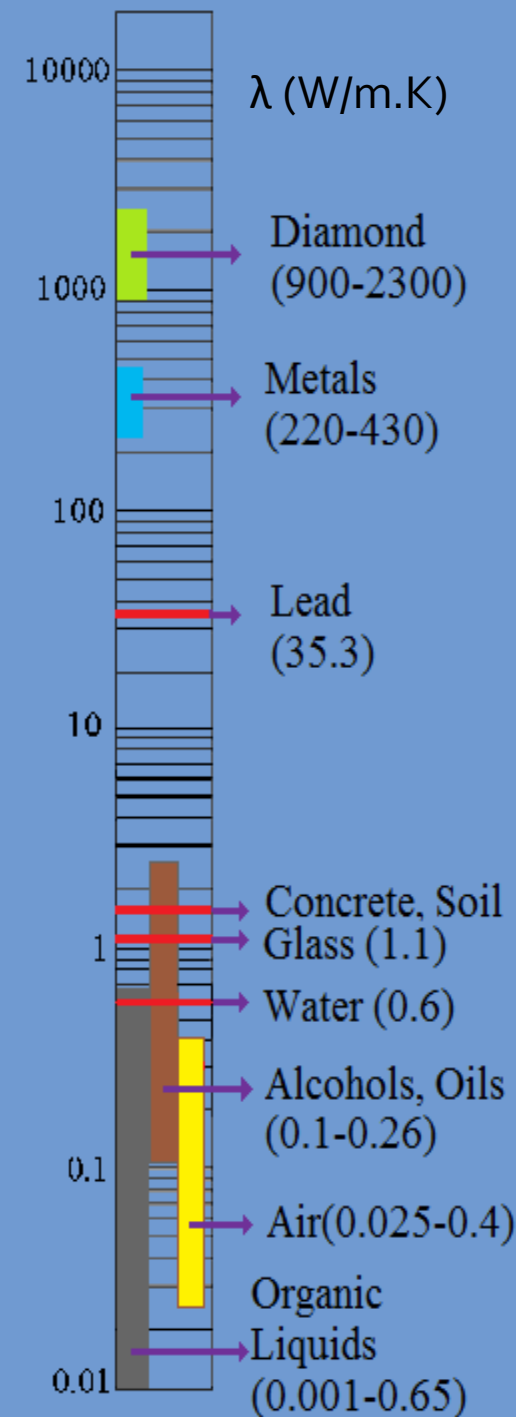
Thermal Conductivity - λ

$$J_q = -\lambda \nabla T$$

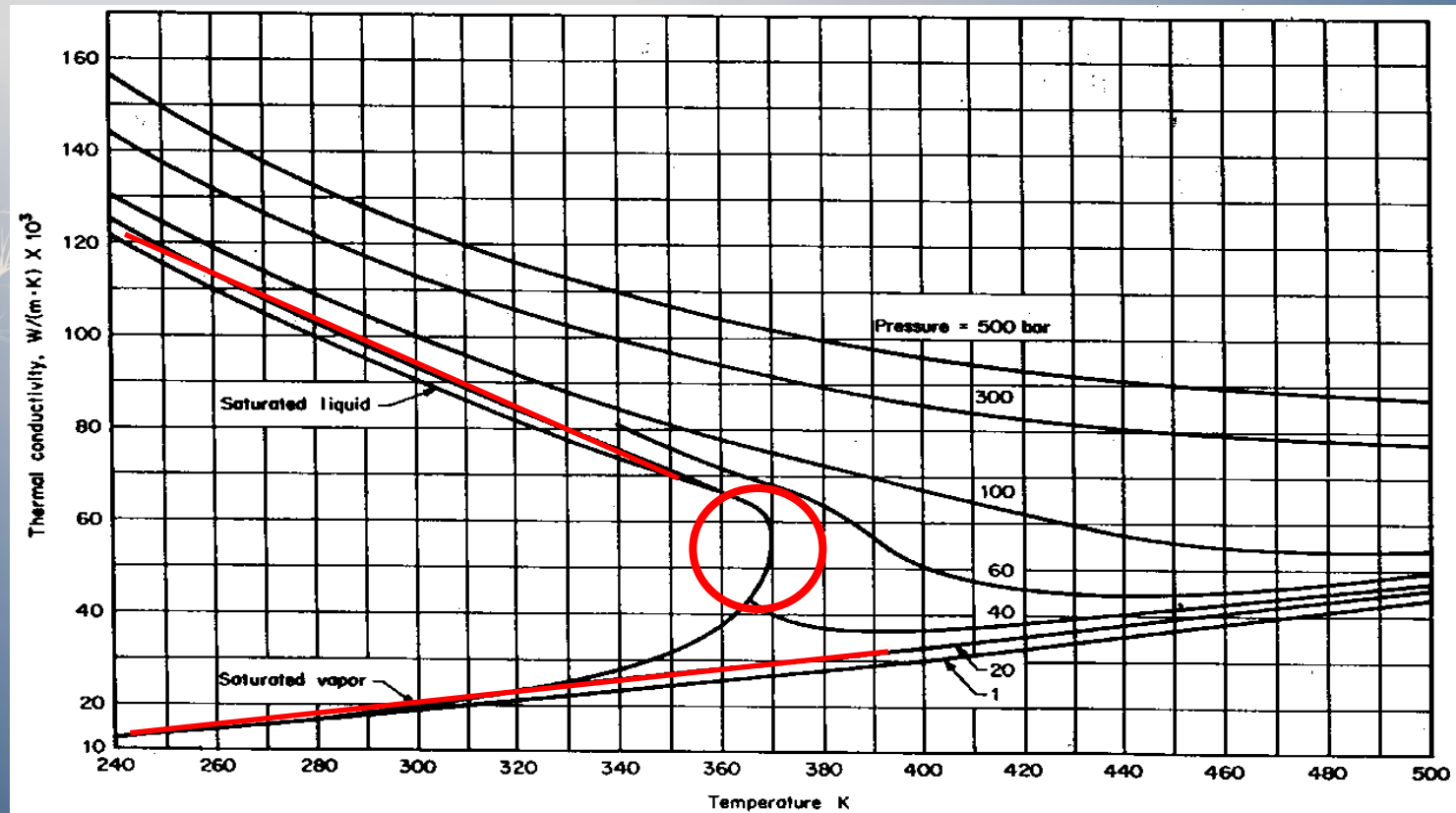
★ Theoretical Contributions and Considerations

★ Critical Enhancement

$$\lambda(\rho_n, T) = \lambda_o(T) + \Delta\lambda(\rho_n, T) + \Delta\lambda_c(\rho_n, T)$$



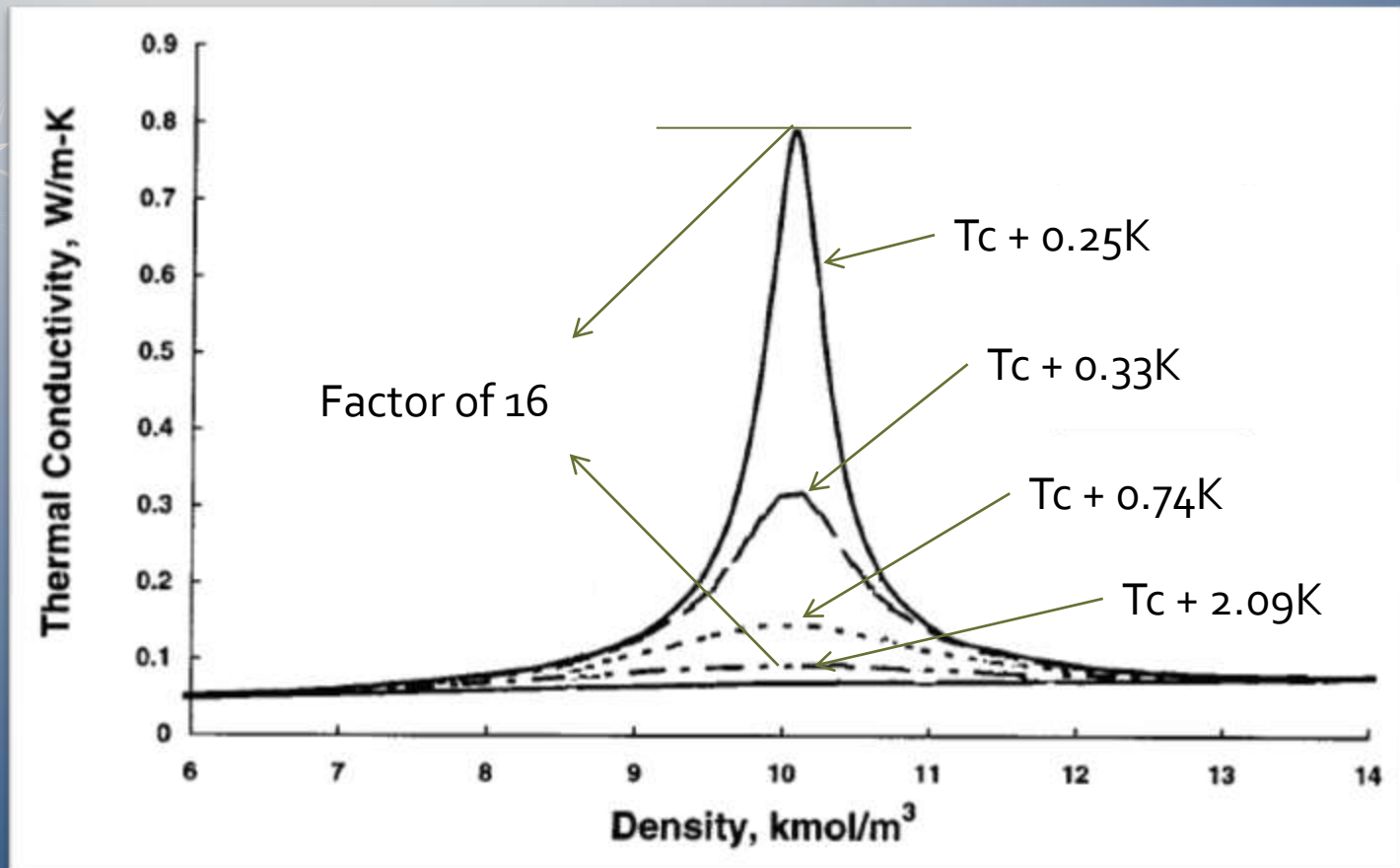
Thermal Conductivity of Propane as f(T,P)



$$\lambda(\rho_n, T) = \lambda_o(T) + \Delta\lambda(\rho_n, T) + \Delta\lambda_c(\rho_n, T)$$

Critical Enhancement

Selected isotherms for CO₂ depicting the critical enhancement phenomenon (Mathias *et al.* 2002)



Correlation and Prediction

✿ Experiments and Data Correlation

✿ Prediction Models

✿ Corresponding States

✿ General Correlations

✿ Family Methods

✿ Group Contribution Method

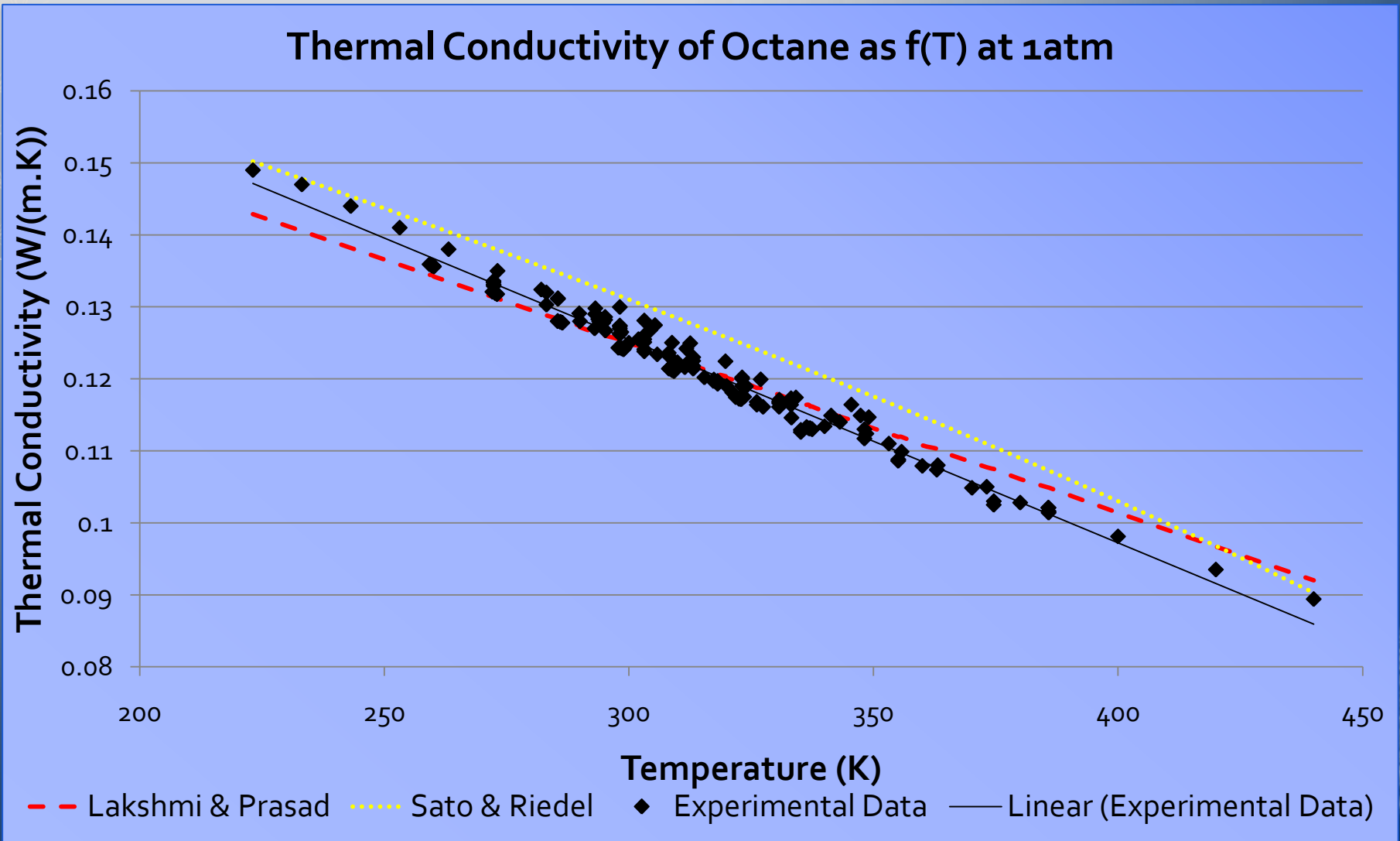
General Correlation Methods

- ✿ Sato and Reidel (1977)
- ✿ Lakshmi and Prasad (1992)

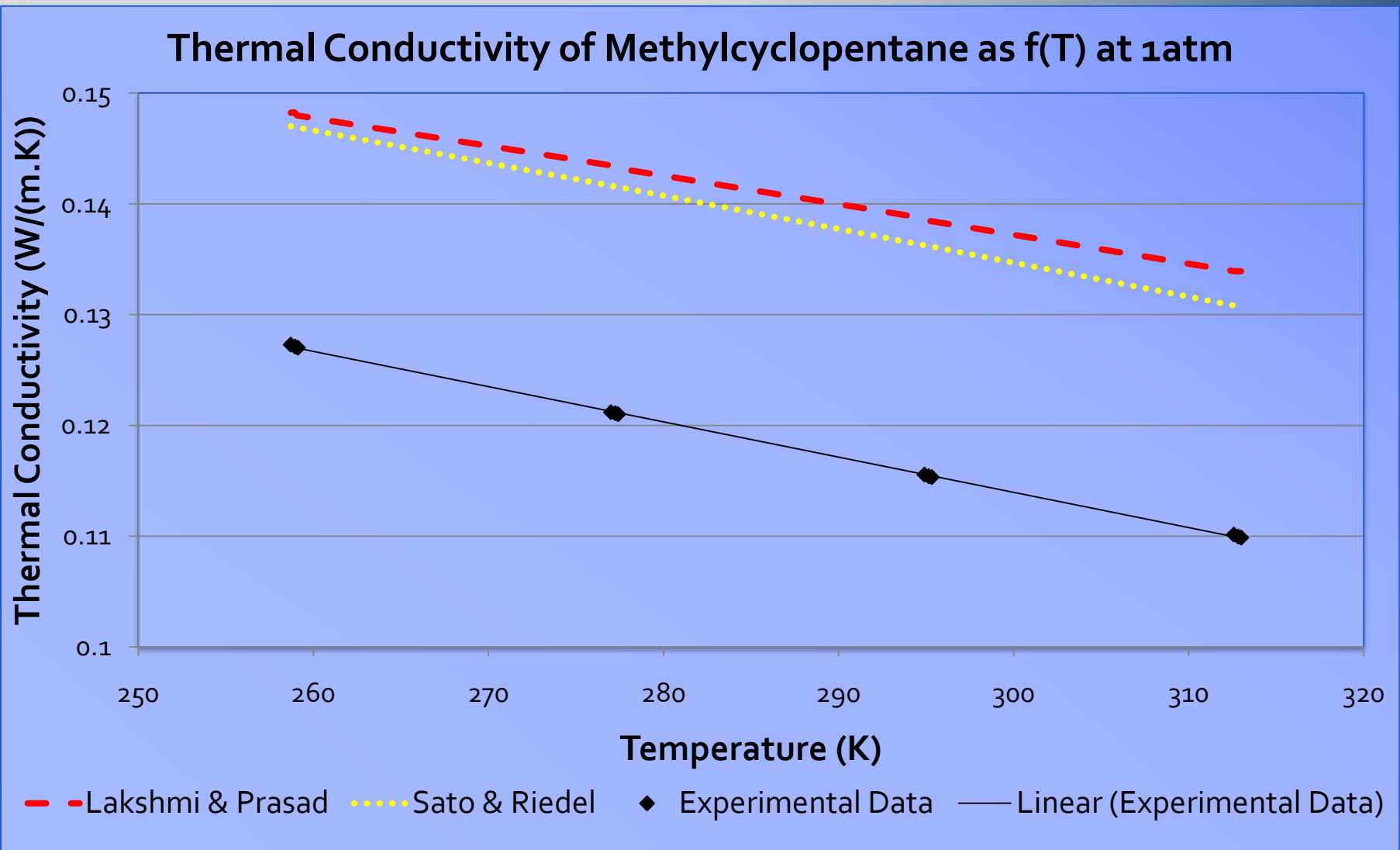
Family Methods

- ✿ Latini *et al.* (1977)

General Correlation Methods



General Correlation Methods



Previous Group Contribution Methods

- ✿ Sakiadis and Coates (1955 , 1957)
- ✿ Robbins & Kingrea (1962)
- ✿ Nagvekar & Daubert (1987)
- ✿ Assael, Charitidou & Wakeham (1989)
- ✿ Sastri and Rao (1993)
- ✿ Rodenbush, Viswanath & Hsieh (1999)
- ✿ Sastri and Rao (1999)

Literature Review & Method Test

Component Classes			
Hydrocarbons	Oxygen Compounds	Ethers	Aldehydes
Aromatic Hydrocarbons	Carboxylic Acids	Esters	Nitrogen Compounds
Halogen Compounds	Alcohols	Ketones	Amines

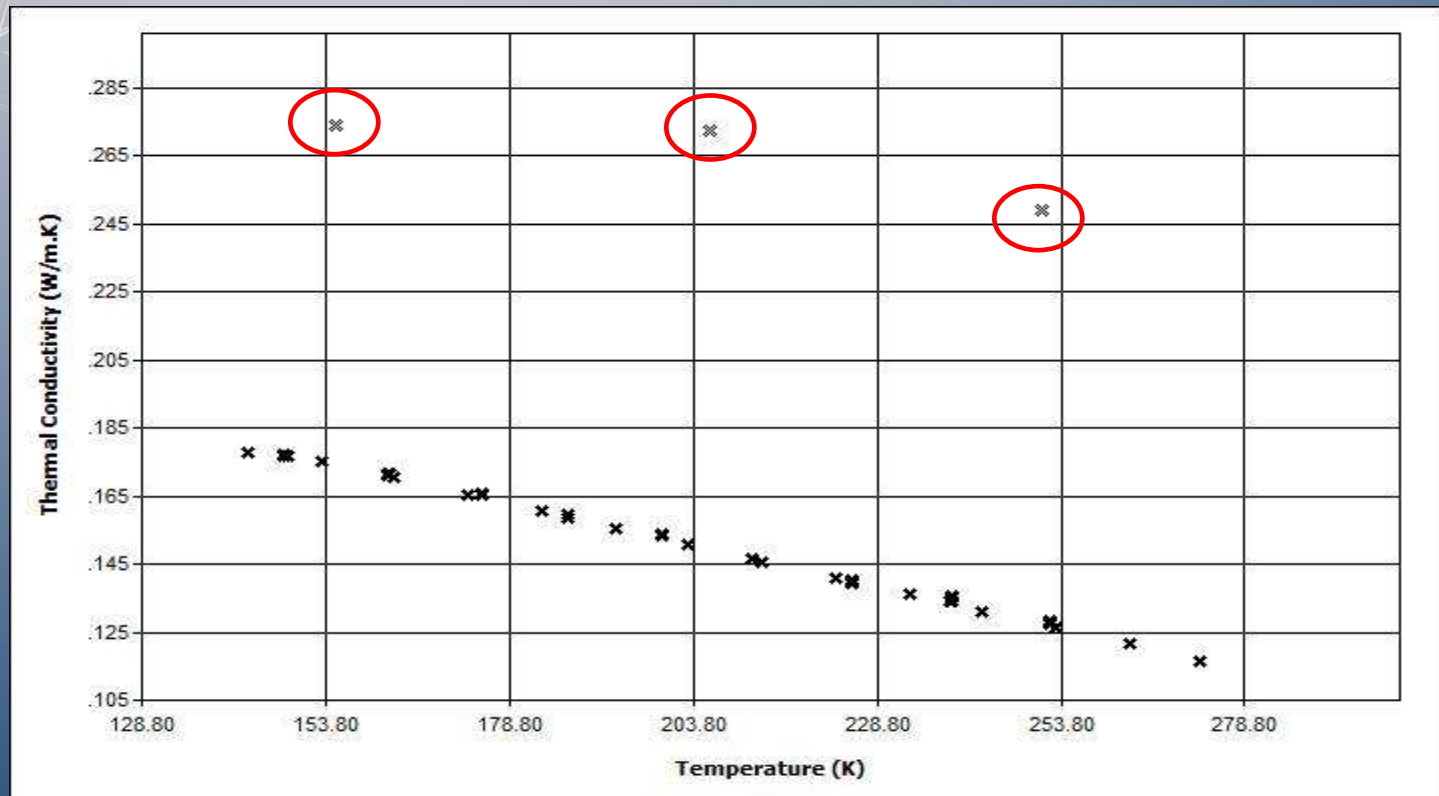
Methods	Sato & Riedel (1997)	Nagvekar & Daubert (1987)	Lakshmi & Prasad (1992)	Sastri & Rao (1993)
RMD (%)	19.81	16.64	23.41	14.11
Number of Components	500	322	500	469

Data Filtration and Validation

DDB – 100 515 data points for 876 components

Figure : Data points for n-butane

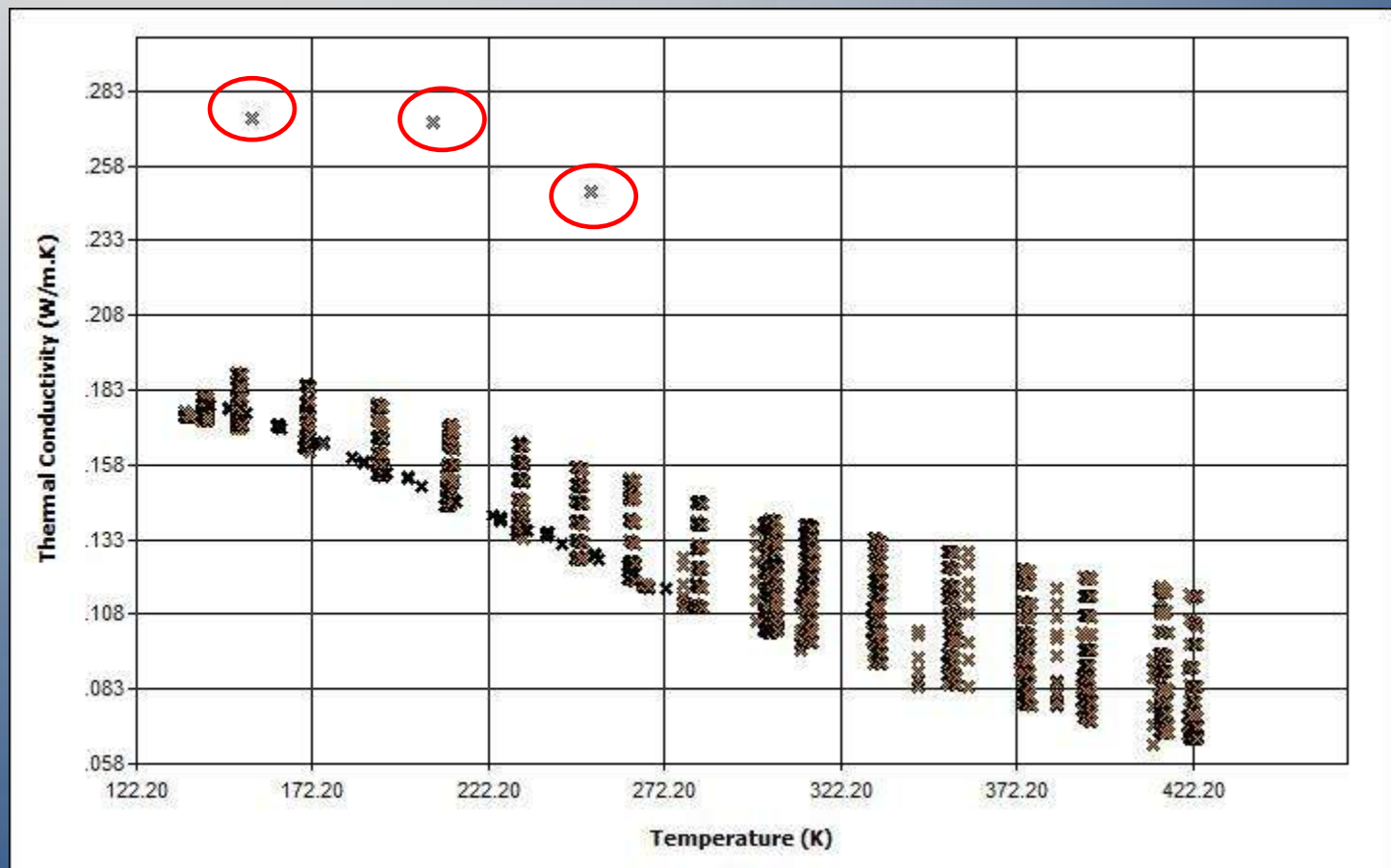
(1atm isobar; $135.75 < T \text{ (K)} < 272.65$)



Data Filtration and Validation

Figure : All experimental data points for n-butane

($135.75 < T \text{ (K)} < 423.61$; $101.325 < P \text{ (kPa)} < 70000$)



Model Idea

Separate group contributions for the 3 parts

$$\lambda(T, P) = \lambda(T_{Ref}) \times f(T - T_{Ref}) \times g(P - 101.3kPa)$$

Reference Value

Temperature Dependence

Pressure Dependence

$$\lambda = \lambda_{REF} + (T - T_{REF}) \times \frac{\partial \lambda}{\partial T} + \lambda_P$$

$$\lambda_P = (P - 101.325) \times \left[\frac{\partial \lambda}{\partial P} + \left([T - T_{REF}] \times \frac{\partial \lambda / \partial P}{\partial T} \right) \right]$$

Software Development

Data Validation

Load/Save
Data Source: Random
Save Changes Exit
Flag Component as Done

Current Verification
DOB Number:
Press DOB # Next DOB #
Organic Group: All
Go to DOB Number: 99
Clear Graph Plot Graph
Plot Non-Press Del. Sing. Points

P (Pa)	A (W/mK)	T (K)	Flag
101.325	0.1597	183.15	0
101.325	0.1568	193.15	0
5000	0.152	196.65	7
30000	0.1586	196.65	7
40000	0.161	196.65	7
101.325	0.1505	196.65	1
50000	0.1633	196.65	7
10000	0.1533	196.65	7
20000	0.156	196.65	7
600	0.1513	203.15	7
10000	0.155	203.15	7
30000	0.1579	203.15	7
30000	0.1608	203.15	7
40000	0.1639	203.15	7
101.325	0.1533	203.15	0
10000	0.1522	213.15	7
600	0.1483	213.15	7
30000	0.1582	213.15	7
40000	0.1615	213.15	7
101.325	0.1498	213.15	0
20000	0.1553	213.15	7
5000	0.145	220.65	7
50000	0.1582	220.65	7
101.325	0.1483	220.65	1
40000	0.1557	220.65	7
10000	0.1467	220.65	7
30000	0.1528	220.65	7
20000	0.1499	220.65	7

Data Flagging
Flag Point Remove Flags
Flag Pressure Flag Duplicates
Thermal Cond. Tol.: 0.0001
Temperature Tol.: 0.05

Plot Saitri & Rao for current DOB number.
Plot Leitch for current DOB number.
Plot Hagelaar & Daubert for current DOB number.

Export Graph as spec
Export 5 Graph as spec

Critical Temp (K): 507.4
Boiling Point (K): 343.1
Crit Press (Pa): 2975

Linear Regression of Data
Linear Regression
TC Ref: m, TC/P: m, TC/P/T: m, TC/T: ADD

Component Name: n-Hexane
Component Name: Hexane
Component Struc: C6H14
Group Name: Hydrocarbons, Alkanes, Chain Alkanes

Data Regression

EXIT Save Changes Flag All 1

Organic Group: All Hexane
DOB Number: 99 CSH14

plot flag = 0 Plot TCN vs T Plot TCN vs P P-FLAG

Bothem Temperatures	P(Pa)	TCN(W/mK)	Flag
196	101.325	0.1597	0
203	101.325	0.1568	0
213	5000	0.152	7
220	30000	0.1586	7
223	40000	0.161	7
233	101.325	0.1505	1
243	50000	0.1633	7
248	10000	0.1533	7
253	20000	0.156	7
262	600	0.1513	7
273	10000	0.155	7
283	20000	0.1579	7
293	30000	0.1608	7
298	40000	0.1639	7
303	101.325	0.1533	0
307	10000	0.1522	7
313	600	0.1483	7
323	30000	0.1582	7
323	40000	0.1615	7
325	101.325	0.1498	0
333	20000	0.1553	7
343	50000	0.149	7
345	101.325	0.1433	1
348			

Export Graph

Linear Reg of TCN-P (> 101)
Parabolic Reg
a
b
c

Linear Reg of TCN-P (> 101)
Linear Reg
m
c

Regression > 101
Avg gradient of all TCN vs P graphs for current DOB num.
Lin Reg

Lin Reg of TCN-T for P = satn
Lin Reg
m: -1.52E-04
c: 0.2242657

- The DDB (Artist)
- Microsoft Office
- SQL & ADO

Future Work

- ✱ Select a regression model and determine empirical parameters for all compounds
- ✱ Evaluation & definition of structural groups
- ✱ Regression for structural or bond contributions
- ✱ Testing using a test set of thermal conductivity data
- ✱ Optimisation of structural or bond contributions

Summary

- ◆ Importance of prediction methods
- ◆ Thermal Conductivity
- ◆ Review of available prediction methods
- ◆ Evaluation of methods
- ◆ Filtration and validation of data from DDB
- ◆ Software
- ◆ Work left to be done

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