CARL VON OSSIETZKY universität OLDENBURG
FAKULTÄT V
MATHEMATIK- UND NATURWISSENSCHAFTEN

UNIVERSITY OF KWAZULU-NATAL

Gruppenbeitrags-Abschätzung von kritischen Daten, Dampfdrücken und Viskositäten komplexer organischer Flüssigkeiten über einen weiten Temperaturbereich

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Timeline

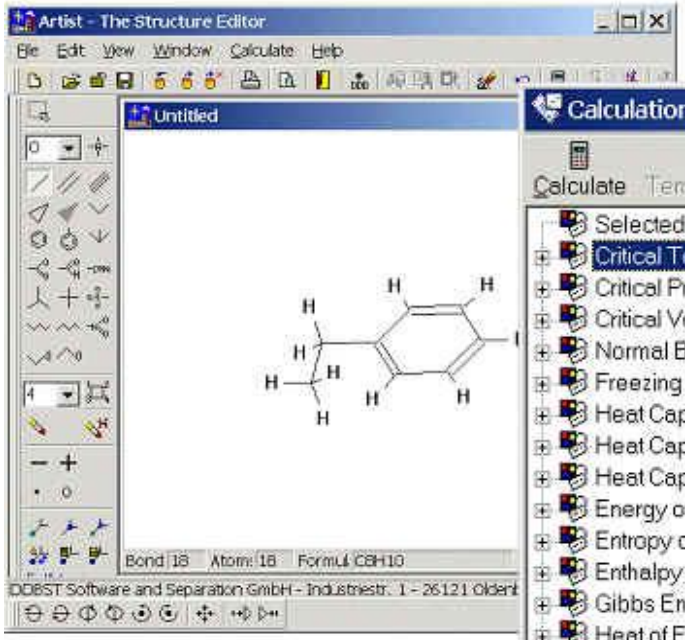
1992	DDB - Pure Component Data Bank
1993	Molecular Structure Editor (ARTIST)
	Automatic Structure Fragmentation (AutoInkr)
	Molecular Structure Data Bank (ChemDB)
1995	Implementation and Test of Group Contribution Methods from Literature (>75)
2002	Normal Boiling Point Estimation (Cordes, Rarey)
2004	Normal Boiling Point Estimation (Nannoolal, Rarey, …)
2005	Critical Data Estimation (publ. 2007)
	Estimation Method Quality
2005	Vapor Pressure Estimation (Thesis Nannoolal)
	Liquid Viscosity Estimation (Thesis Nannoolal)
2007	Enhanced Vapor Pressure Estimation
2008	Thermal conductivity and Surface Tension Estimation

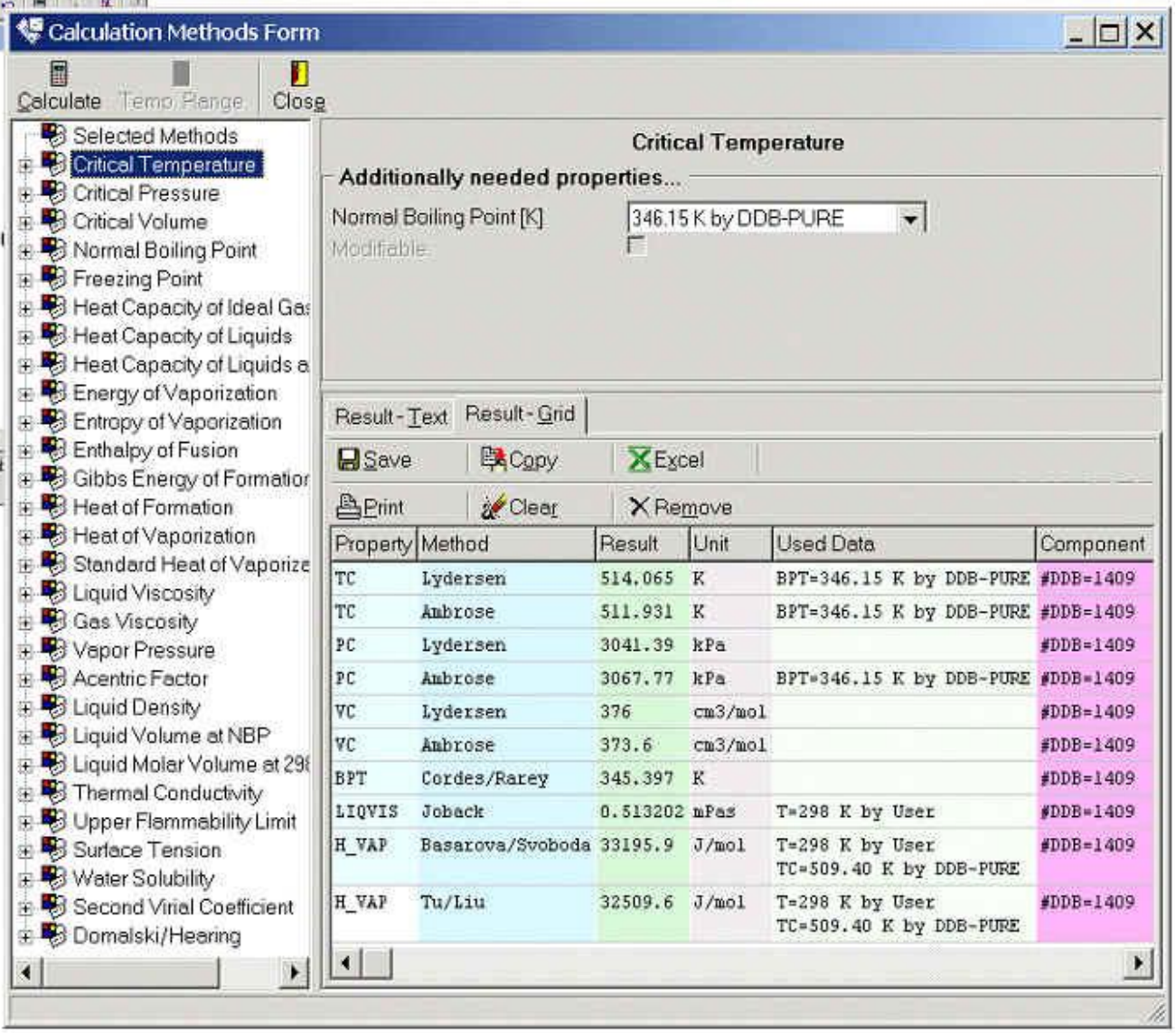
DDB - Pure Component Data Bank (February 2007)

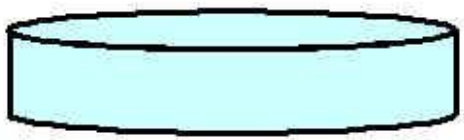
	Compounds	References	Sets	Data Tuples
Vapor Pressure	7144	6784	26339	172355
Critical Data	1049	932	3481	3488
Viscosity	2956	2826	17573	107659
Density	7801	6428	42289	304262
Melting Point	5922	2913	13196	14694
Heat Capacity	3952	2787	13734	239200
Enthalpy of Vaporization	2525	1081	5120	12036
Enthalpy of Fusion	1596	941	2412	2489
Thermal Conductivity	815	945	9102	95833
Surface Tension	2166	682	4841	21691
Entropy	1520	941	2700	9563
Std. Heat of Combustion	1378	433	1598	1607
Std. Heat of Formation	2912	1251	4186	4269
Speed of Sound	549	376	3318	27477
G-function	1208	563	1898	28374
…				
Total	16692	20237	157366	1078128

Molecular Structures, Fragmentation, Estimation

ARTIST – Structure Editor







approx.

22 500

structures

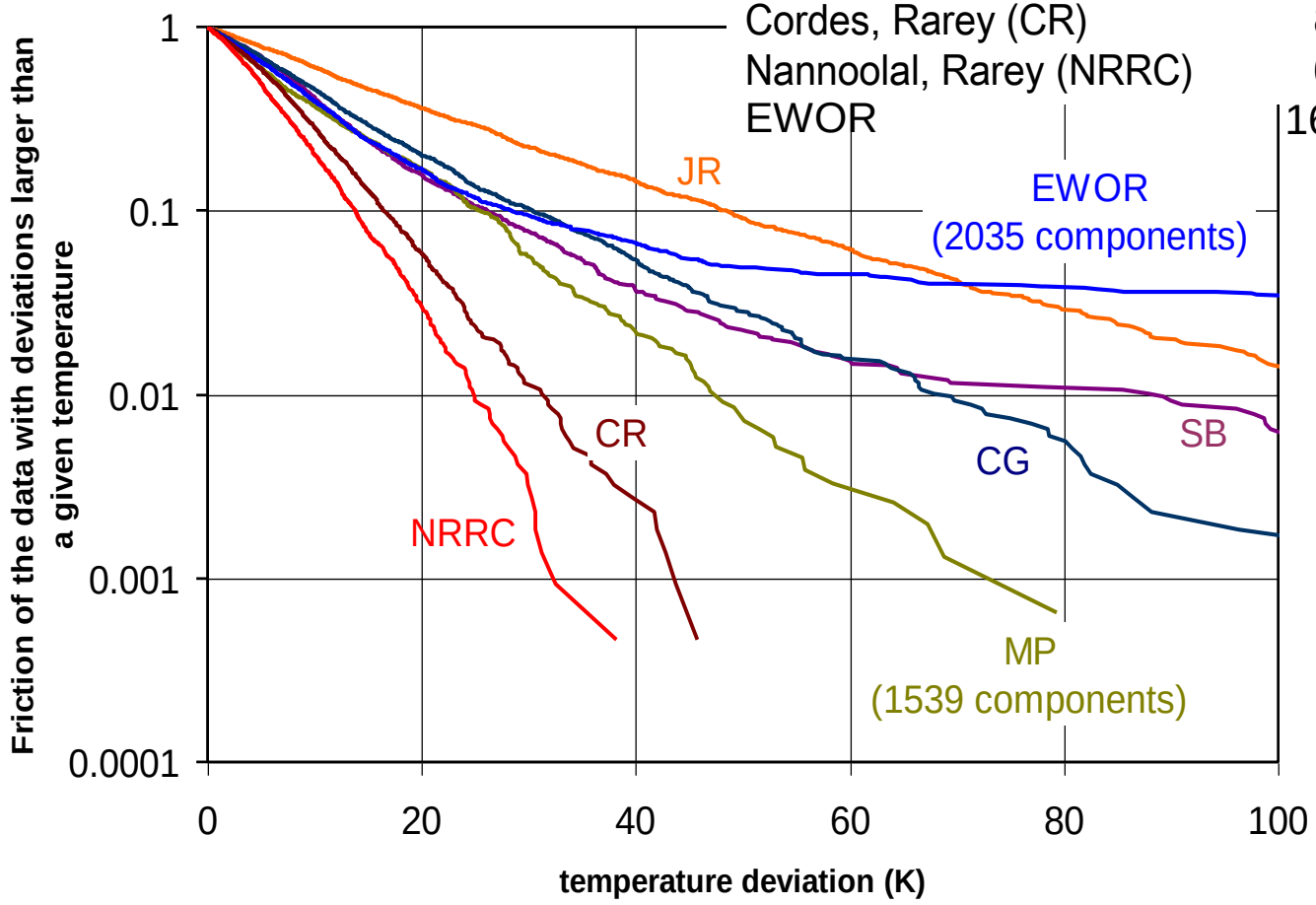
Normal Boiling Point Estimation

Method	Mean Absolute Deviation [K] (Number of Components)	Data Points / Parameters
Joback, Reid	21.42 (2506)	438/41 = 10.7
Stein, Brown	14.46 (2579)	≈ 10000/90 ≈ 110
Gani, Constantinou	13.25 (2259)	392/120 = 3.3
Marrero-Pardillo	10.23 (1665)	507/165 = 3.1
EWOR	16.82 (2280)	1141/304 = 3.8
Cordes/Rarey	8.16 (2758)	2550/96 = 26.6
Nannoolal/Rarey/ Ramjugernath/Cordes	6.52 (2812)	2812/214 = 13.1

Normal Boiling Point Estimation, Integral Deviation

Part of the data with deviations larger than a given temperature

	AAD [K]	components
Joback, Reid (JR)	21.42	2506
Stein, Brown (SB)	14.46	2579
Constantinou, Gani (CG)	13.25	2259
Marrero, Pardillo (MP)	10.23	1665
Cordes, Rarey (CR)	8.16	2758
Nannoolal, Rarey (NRRC)	6.5	2812
EWOR	16.82	2280



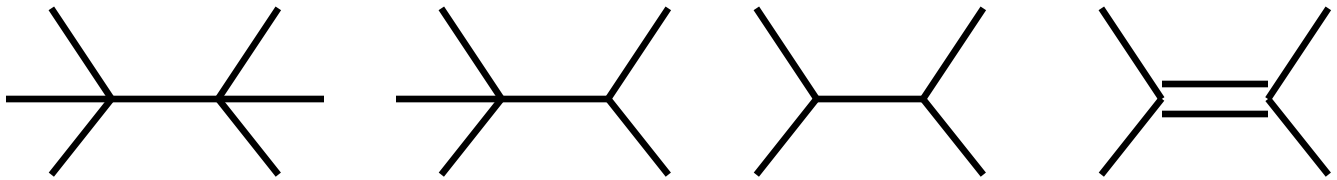
Special Considerations

It has to be taken into account whether:

- a group is part of a ring (r) or a chain (c)
- a group is part of an aromatic system (a)
- a group has a strongly electronegative neighbor (N, O, F, Cl) (e)

It is mostly of no importance whether the neighbor of a group is C or Si.

Sterically hindered isomers require a special correction.



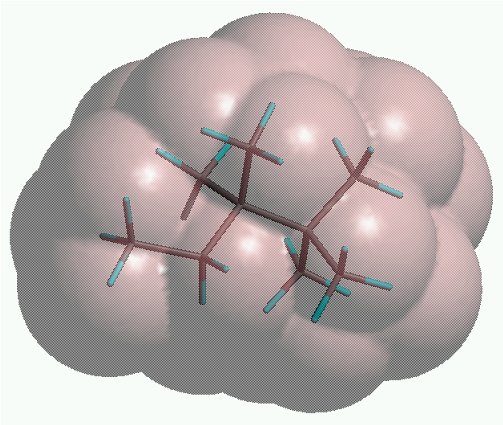
Conjugated carbonyl groups (aldehyde, ketone, carboxylic acid, ester) require a special correction (C=C-C=O).

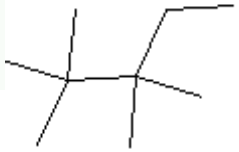
Hydrogen bonding group contributions are usually not additive.

Isomer Problem

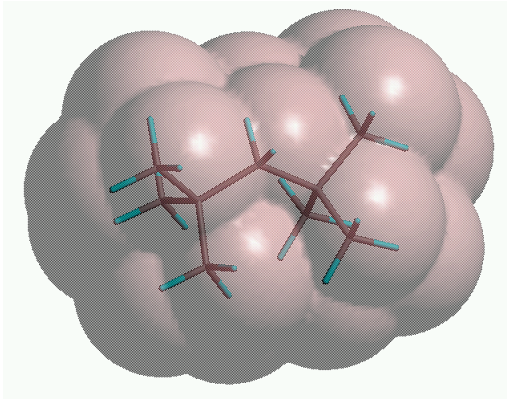
6432 – $T_{b,\,exp}$ – 413.4K – VdW Surface – 161 Å^2
6433 – $T_{b,\,exp}$ – 395.5K – VdW Surface – 171 Å^2

$\Delta T = 17.9K$





DDB# 6432



DDB# 6433

$$T_b = \frac{\Delta h_v}{\Delta s_v}$$

$\Delta s_v \approx 0.8\%$ $\Delta h_v \approx 5.4\%$ significantly different polarisability

Old: 6432 – $T_{b,\,est}$ – 390.9K	6433 – $T_{b,\,est}$ – 390.9K
New: 6432 – $T_{b,\,est}$ – 412.8K	6433 – $T_{b,\,est}$ – 391.8K

Results for Multifunctional Components

Hydrogen bonding group contributions are usually not additive.

	CG	JR	MP	SB	CR	New*
Alkane Diols	24.3K	30.9K	18.4K	23.6K	15.9K	24.4K

With OH-OH Interaction Parameter – **Average Deviation : 7.1K**

	CG	JR	MP	SB	CR	New*
Glycerol	71.2K	18.8K	17.7K	59.3K	42.8K	52.1K

With OH-OH Interaction Parameter – **Deviation : 8.1K**

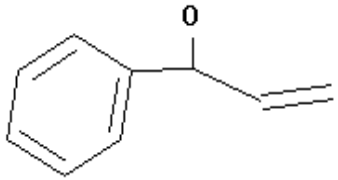
	GC	JR	MP	SB	CR	New*
OH - NH2	15.7K	15.0K	18.2K	27.8K	18.4K	32.1K

With OH-NH2 Interaction Parameter – **Average Deviation : 5.3K**

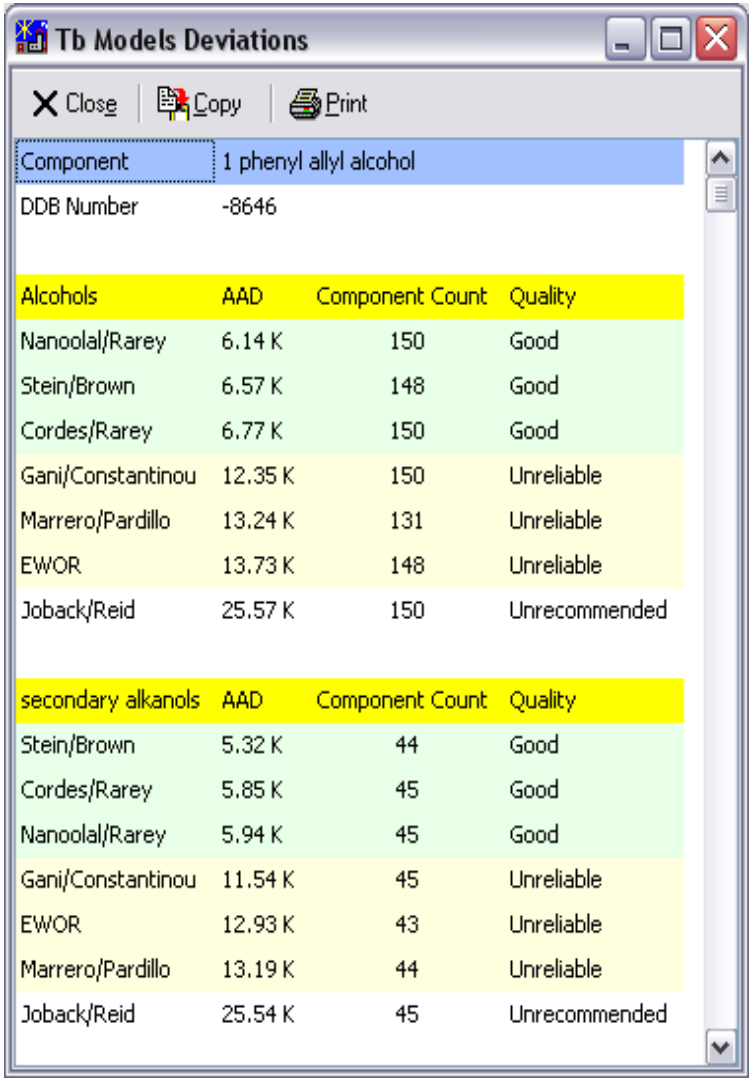
* regressed to monofunctional components without interaction groups.

Expert System for Estimation Reliability

- More than 180 substance classes
- Substance class of a component can be derived from fragmentation
- Extended tables for the deviations of different models for the different substance classes are under development.



exp.	488.7 K	deviation
Cordes/Rarey	495.7 K	7.0 K
Nannoolal/Rarey	494.9 K	6.2 K
Stein/Brown	495.1 K	6.4 K
Joback	520.6 K	31.9 K
Gani/Constantinou	499.1 K	10.4 K
Marrero/Pardillo	491.3 K	2.6 K
EWOR	529.8 K	41.1 K



Model Equations

Liquid Vapor Pressure

$$\log\left(\frac{P^S}{1atm}\right) = (4.1012 + dB)\left(\frac{T_{rb} - 1}{T_{rb} - \frac{1}{8}}\right) + \left[\frac{0.75407}{1 + 7 \cdot \exp\left(\frac{201}{T - 91}\right)} - 1\right]$$

alkanol correction

$$T_B = \frac{SGC}{n^a + b} + c \qquad dB = SGC - a$$

Critical Data

$$T_c = T_b\left(b + \frac{1}{a + SGC^c}\right)$$

$$\frac{P_c}{kPa} = \frac{M^b}{(a + SGC)^2}$$

$$\frac{V_c}{10^{-6} m^3 mol^{-1}} = \frac{SGC}{n^a} + b$$

Liquid Viscosity Estimation

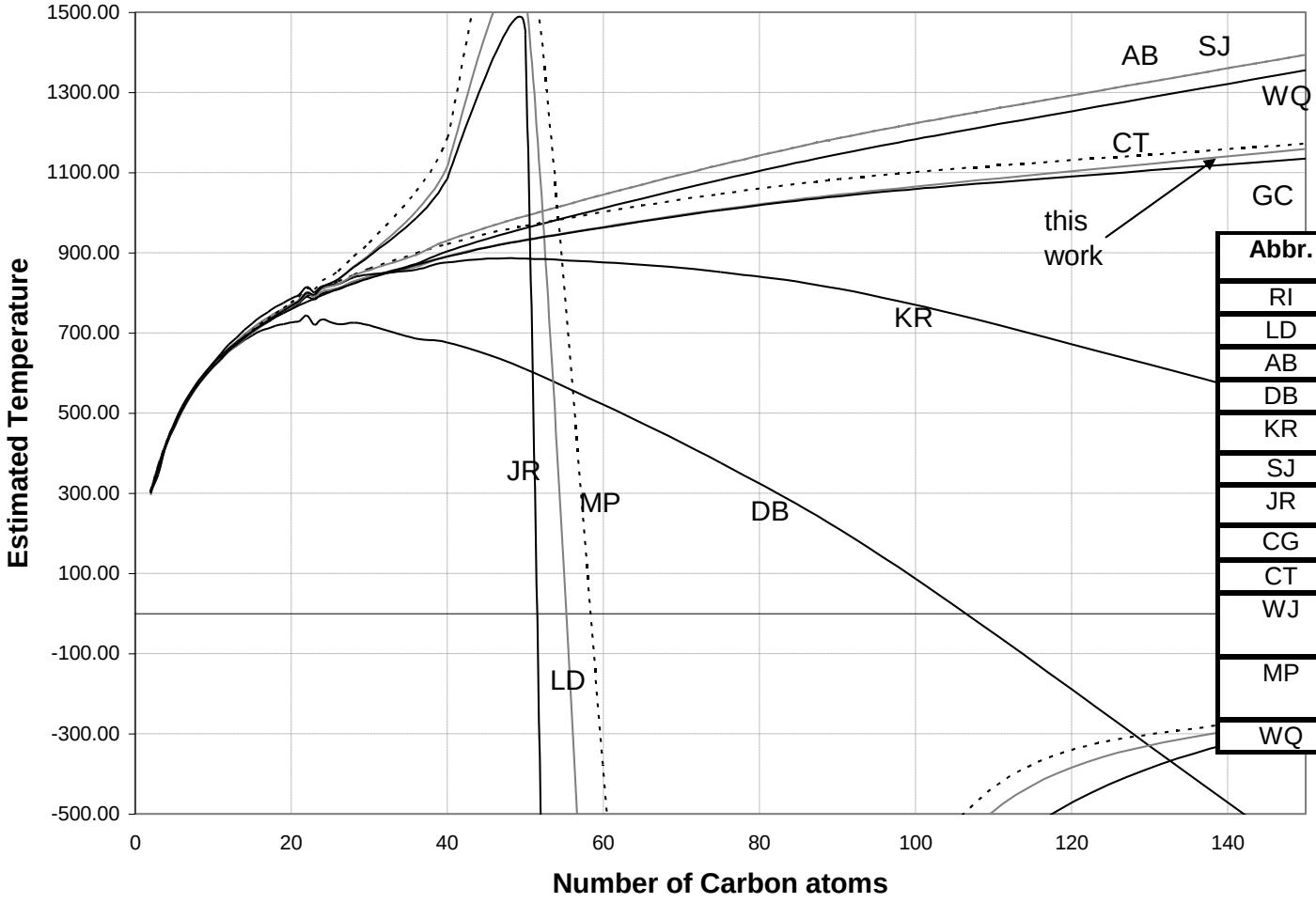
$$\ln\left(\frac{\mu}{1.3cP}\right) = -dBv\left[\frac{T - T_v}{T - \frac{T_v}{16}}\right]$$

$$dBv = \frac{SGC}{n^a + b} + c \qquad T_v = a \cdot T_b^{0.5} + \frac{SGC^b}{n^C + d} - e$$

Sum of **G**roup **C**ontributions

$$SGC = \sum_{i=1}^{n} \nu_i \Delta_i + \frac{1}{n} \sum_{i=1}^{m} \sum_{j=1}^{m} \frac{C_{i-j}}{m - 1}$$

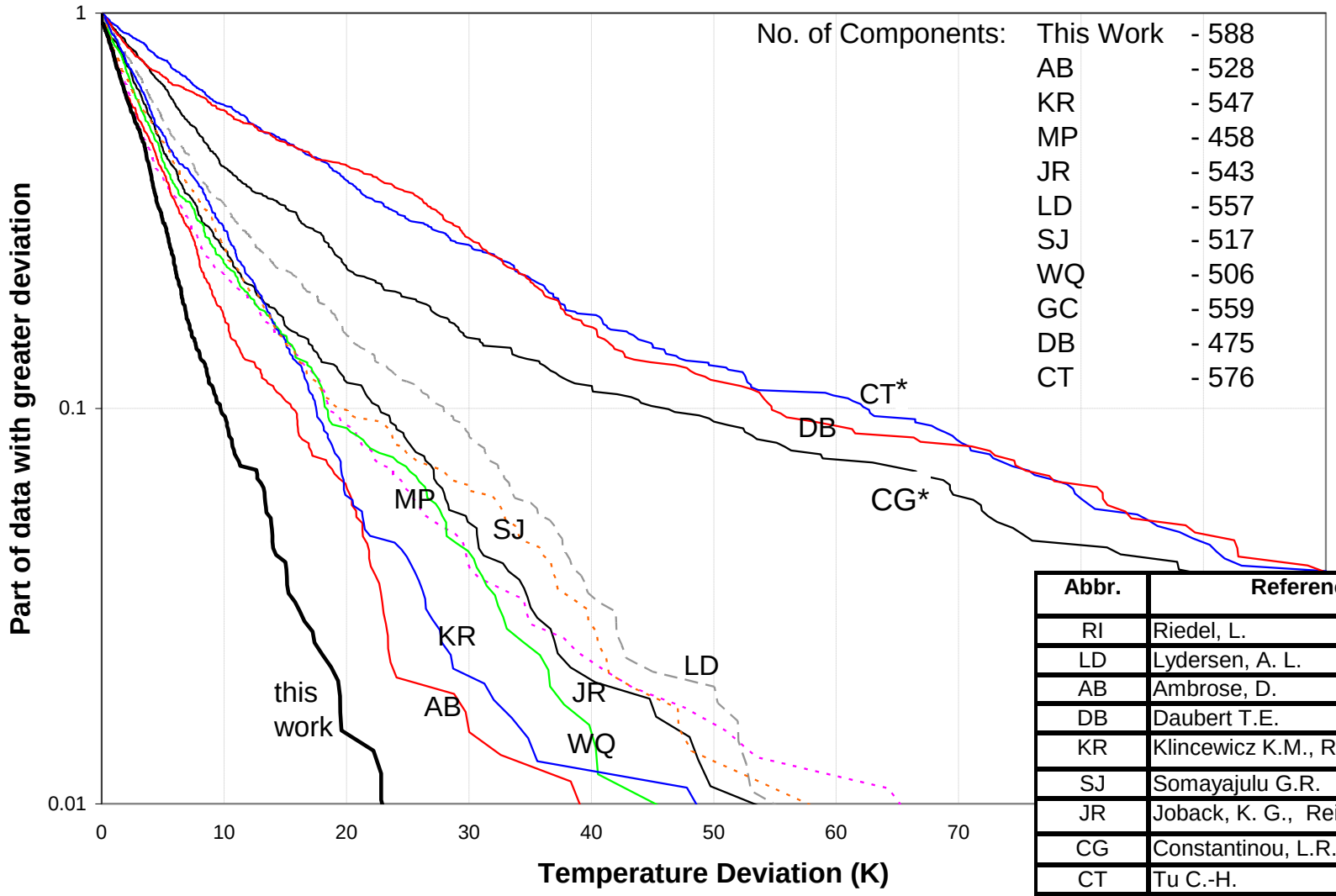
Critical Temperature Estimation (n-Alkanes)



Abbr.	Reference
RI	Riedel, L.
LD	Lydersen, A. L.
AB	Ambrose, D.
DB	Daubert T.E.
KR	Klincewicz K.M., Reid R.C.
SJ	Somayajulu G.R.
JR	Joback, K. G., Reid, R. C.
CG	Constantinou, L.R., Gani, R.
CT	Tu C.-H.
WJ	Wilson, G.M., Jasperson, L.V.
MP	Marrero-Morejon, J., Pardillo-Fontdevila, E.
WQ	Wen X., Quiang Y.

Estimated critical temperature for n-alkanes as function of the number of carbon atoms from different group contribution methods (AB and SJ overlap).
(this work: Nannoolal,Y., Rarey, J., Ramjugernath, D., Fluid Phase Equil., accepted for publication)

Critical Temperature Estimation, Integral Deviation



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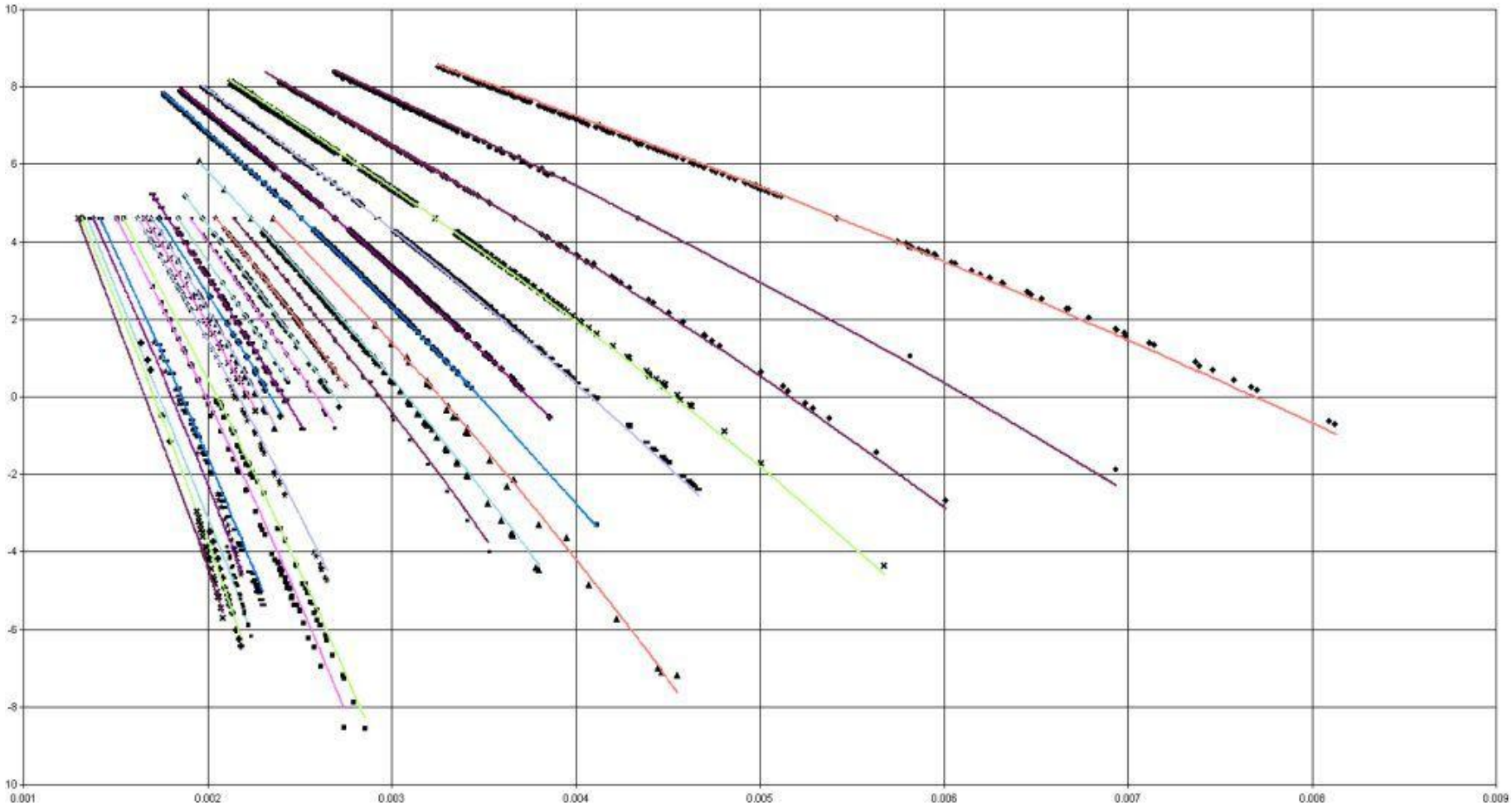
* no normal boiling temperature required

Critical Property Deviations

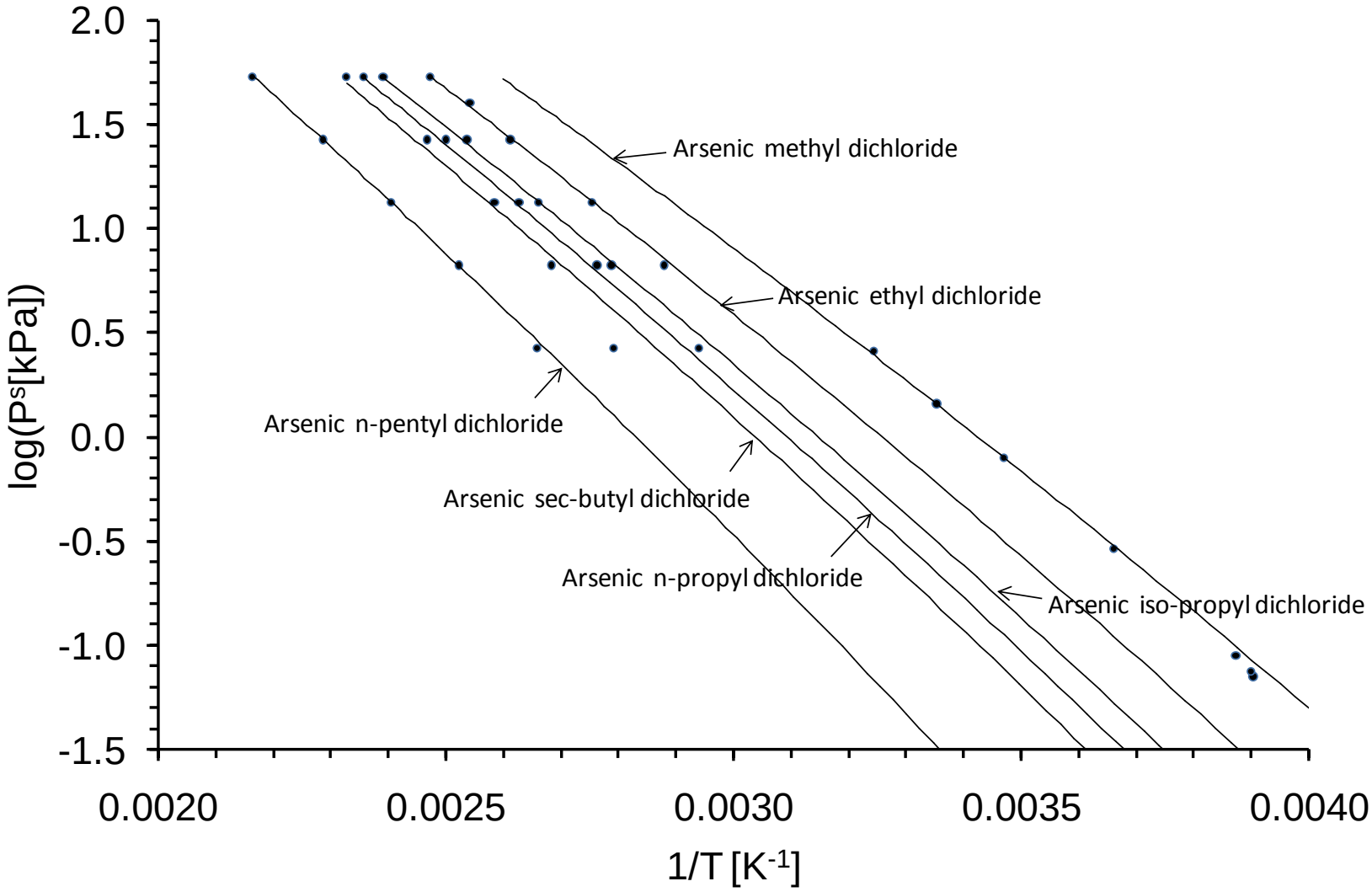
Methods	T_c			P_c			V_c		
	Number of Com-ponents	Average Absolute percentage Error	Absolute Average Error (K)	Number of Com-ponents	Average Absolute percentage Error	Absolute Average Error (kPa)	Number of Com-ponents	Average Absolute percentage Error	Absolute Average Error (cm^3/mol)
This work	588	0.74	4.31	486	2.96	99.82	348	1.79	6.40
Ambrose	528	1.07	6.00	412	7.03	252.46	242	3.99	19.41
Marrero Pardillo	458	1.21	7.79	381	6.04	208.92	248	3.36	16.11
Klincewicz/Reid	547	1.27	7.83	452	7.57	245.67	319	3.96	17.87
Wen/Qiang(Tb)	506	1.26	7.79						
Joback	543	1.41	8.75	452	7.11	238.20	314	3.73	16.49
Somayajulu	517	1.44	8.39	438	9.51	294.59	307	4.14	20.08
Lydersen	557	1.71	10.65	474	7.07	227.53	327	5.37	30.67
Daubert	475	3.87	23.91	352	7.00	252.45			
Methods not requiring T_b:									
Wen/Qiang	506	2.97	16.73	421	5.67	196.81	294	4.99	22.05
Gani, Constantinou	559	4.07	17.19	410	7.12	247.84	277	4.81	22.84
Chein-Hsiun Tu	572	4.26	23.31						

Vapor Pressure Estimation (n-Alkanes)



Vapor Pressure Estimation (Arsine Compounds)

Log(P) vs. 1/T for Several Arsine Compounds Together with Estimation Results.



Development of the Liquid Viscosity Method

Regression of T_v and *dBv* to viscosity data for each component separately.

$$\ln\left(\frac{\mu}{1.3cP}\right) = -dBv\left[\frac{T - T_v}{T - \frac{T_v}{16}}\right]$$

Calculation and examination/revision of *dBv* for each data point using fixed T_v.

Averaging of *dBv* for each component.

Group contribution regression of *dBv.*

Objective function improved?

yes

Regress new T_v for each component using group contribution estimate of *dBv.*

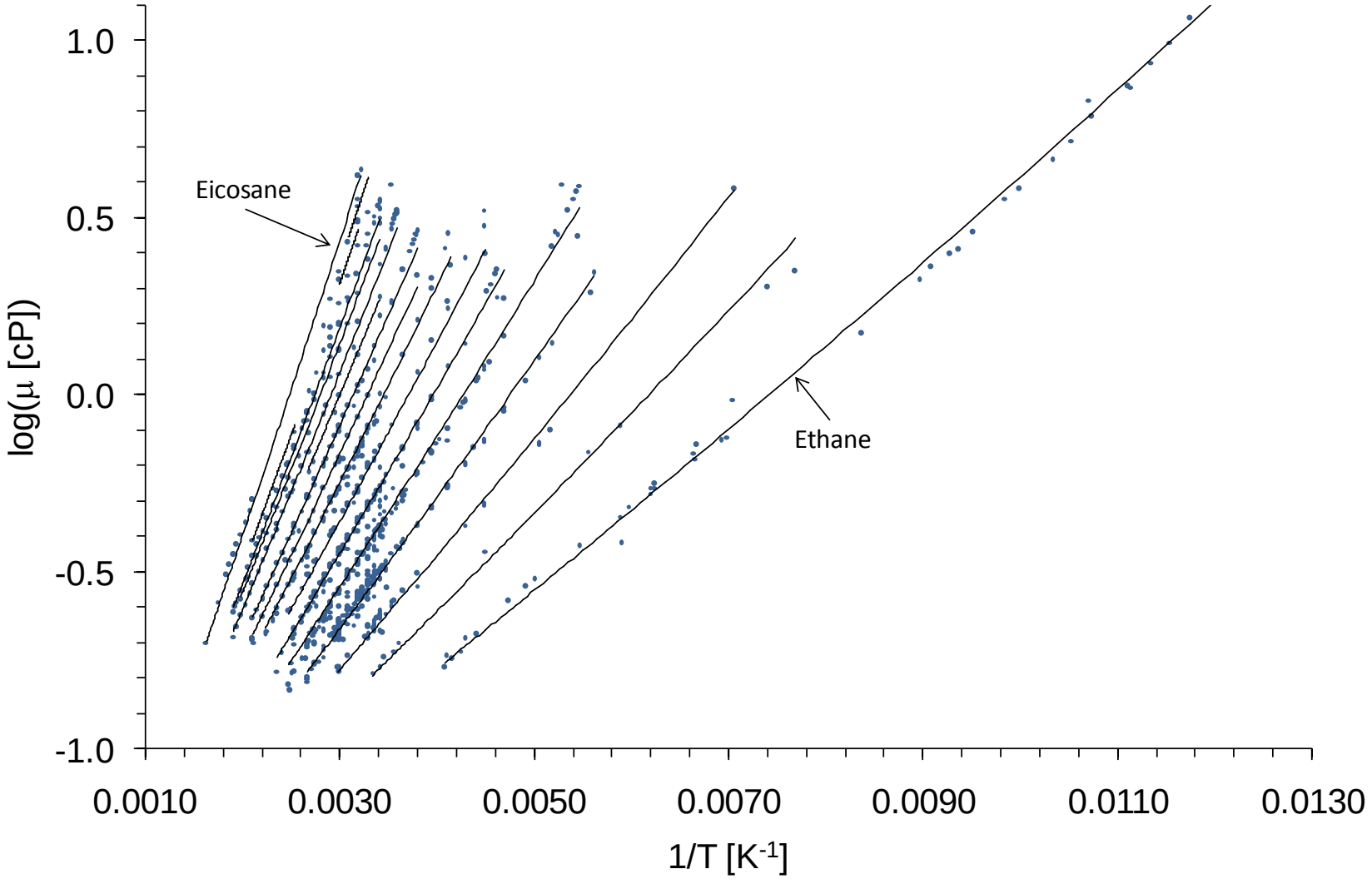
no

exit

The method requires knowledge of a reference temperature T_v, at which the viscosity of a component is equal to the reference viscosity. This often requires extrapolation far outside the range of available experimental data.

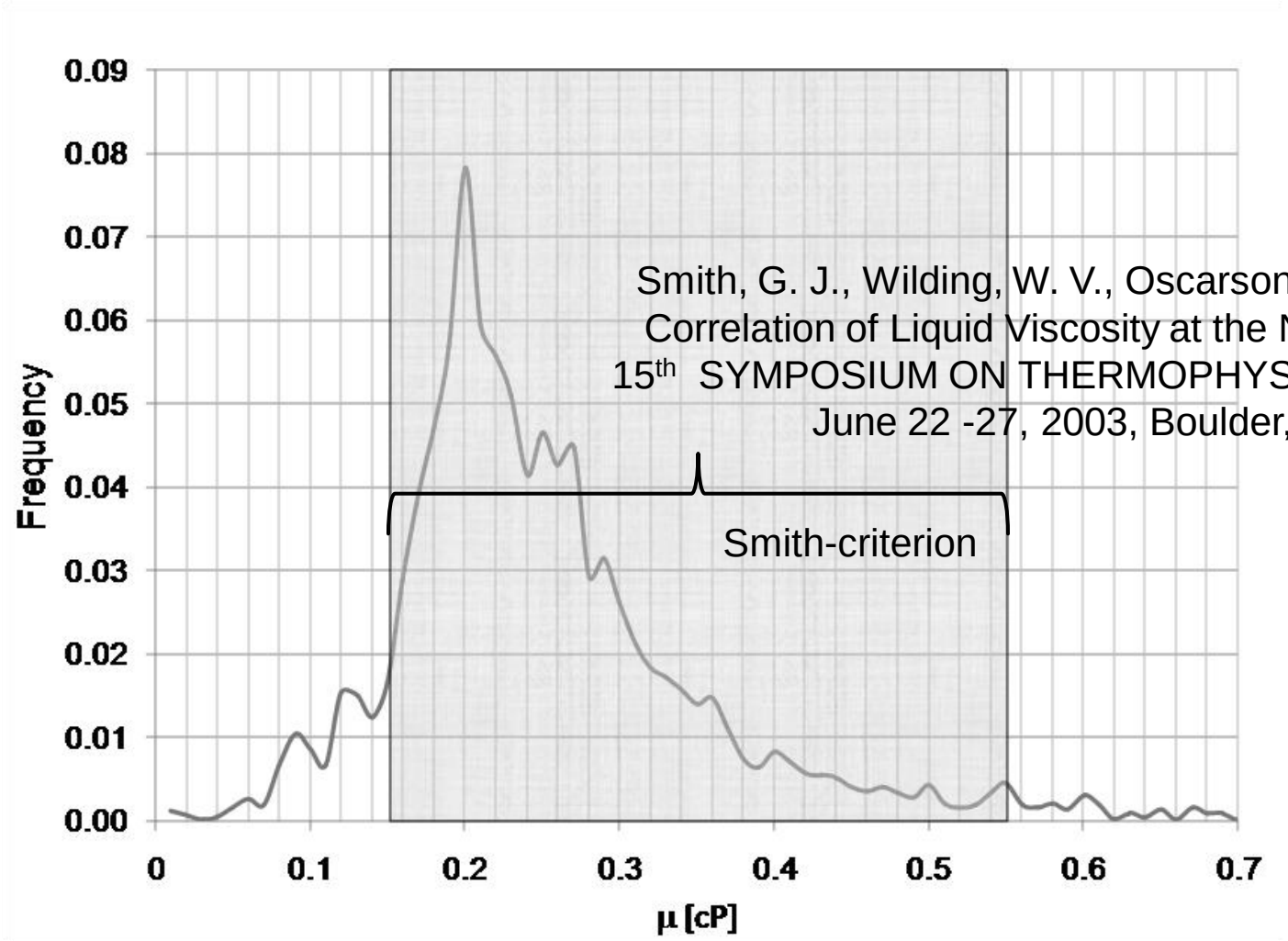
Viscosity Model - Results

Experimental and Estimated Liquid Viscosities for n-Alkanes (Ethane to Eicosane) Using Adjusted Reference Temperatures



Viscosity Model Test

Frequency of estimated liquid viscosity values at the normal boiling point for a set of 4192 components (data taken from the DDB, estimated T_v and dB_v)



Smith, G. J., Wilding, W. V., Oscarson, J. L., Rowley, R. L.
Correlation of Liquid Viscosity at the Normal Boiling Point
15th SYMPOSIUM ON THERMOPHYSICAL PROPERTIES,
June 22 -27, 2003, Boulder, CO, USA

Vapor Pressure Estimation

Mean Relative Deviation (Normal Boiling Point plus estimated slope)

	number of components	extremely low pressure	low pressure	medium pressure	high pressure	average
Estimation (%)	1663	40.4^{1030}	11.0^{20243}	2.8^{37615}	5.7^{11610}	6.2^{70498}
Correlation (%)	1663	43.7^{1017}	7.6^{19929}	1.8^{37374}	4.8^{11607}	4.5^{69927}

(Number of data points as Superscript)

Liquid Viscosity Estimation

Mean Relative Deviation (One data point plus estimated slope)

	number of components	extremely low pressure	low pressure	medium, high pressure	average
Estimation (%)	829	5.6^{1363}	3.5^{7896}	2.5^{4431}	3.4^{13690}
Correlation (%)	829	2.6^{1363}	1.6^{7896}	1.8^{4431}	1.8^{13690}

(Number of data points as Superscript)

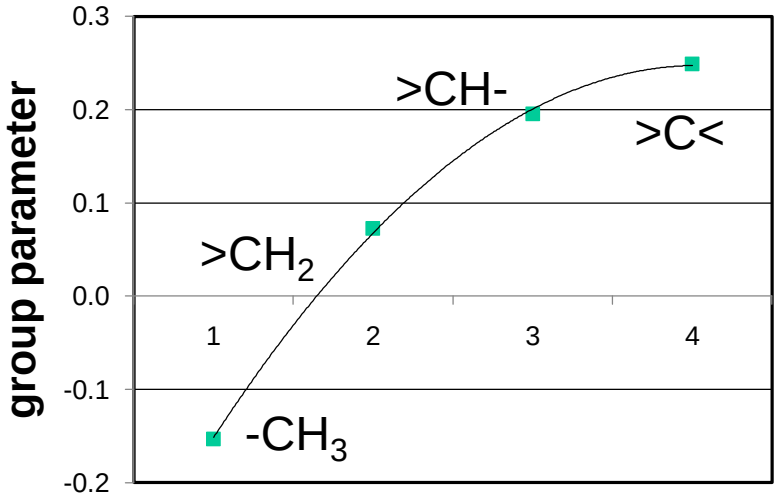
15.3% Mean Relative Deviation (Estimated T_v and *dBv*)

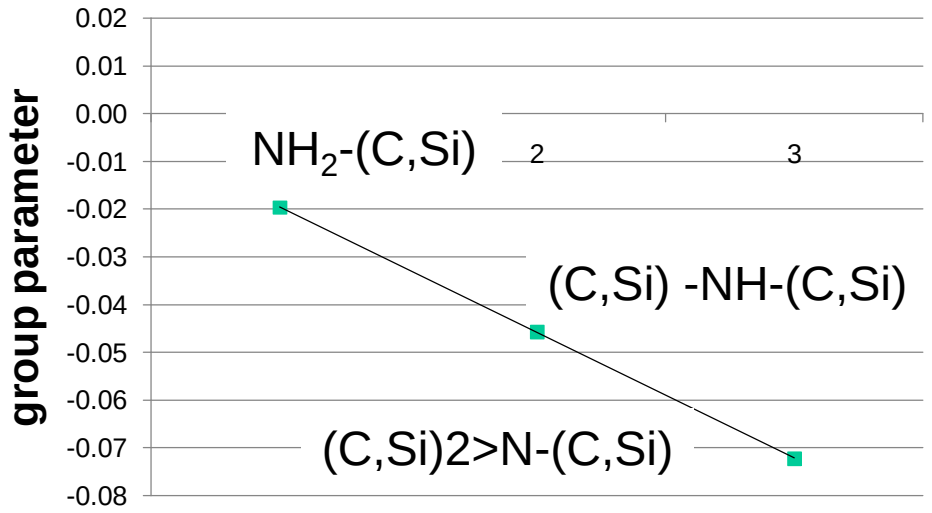
Van Velzen: 92.8 % for 670 components (11,115 data points)

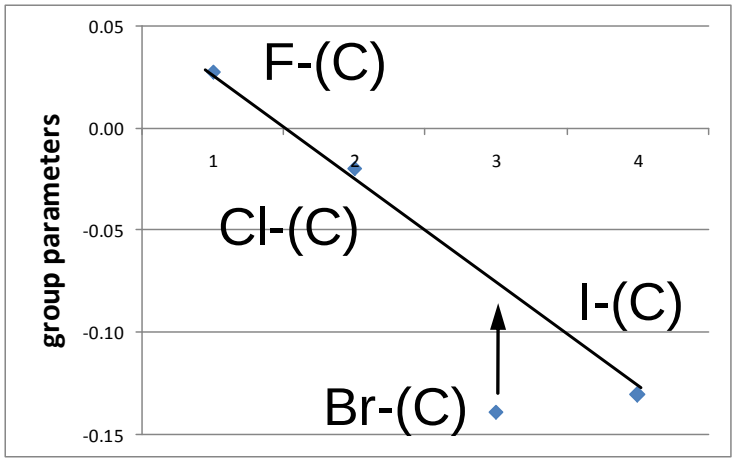
extremely low pressure - < 0.01kPa
low pressure - 0.01kPa >= P =< 10kPa
medium pressure - 10kPa < P =< 500 kPa
high pressure > 500 kPa

Physically Realistic Group Parameters

Group Parameters of the Enhanced Vapor Pressure Method







Natura non facit saltum (Nature does nothing in jumps)

New Estimation Methods

Estimation Methods by Nannoolal, Rarey, Ramjugernath:

- Normal Boiling Point (recommended by DIPPR)
- Saturated Liquid Vapor Pressure
- Critical Data
- Saturated Liquid Viscosity

Under Development:

- Enhanced Normal Boiling Point / Vapor Pressure Method
- Activity of Complex Molecules in Simple Solvents (Solubility, ...)

Planned:

- Thermal Conductivity Estimation
- Surface Tension Estimation
- Extension to Solid Phase Properties if Reliable Algorithm for Molecular Symmetry can be Developed

Available in DDBSP - Artist

Partly in DIADEM (DIPPR Estimation Software (BYU))

Acknowledgement

Finally I wish to thank

- Prof. J. Gmehling for supporting this independent work.
- South African National Research Foundation (International Science Liaison and Thuthuka Programmes) for financial support.
- BMBF (WTZ-Project) for financial support.
- DDBST GmbH, especially Mr. W. Cordes, for providing access to the DDB and software support.
- and last not least the audience……..