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Estimation of Vapour Pressures of Organic Liquids using Group Contributions and Group Interactions

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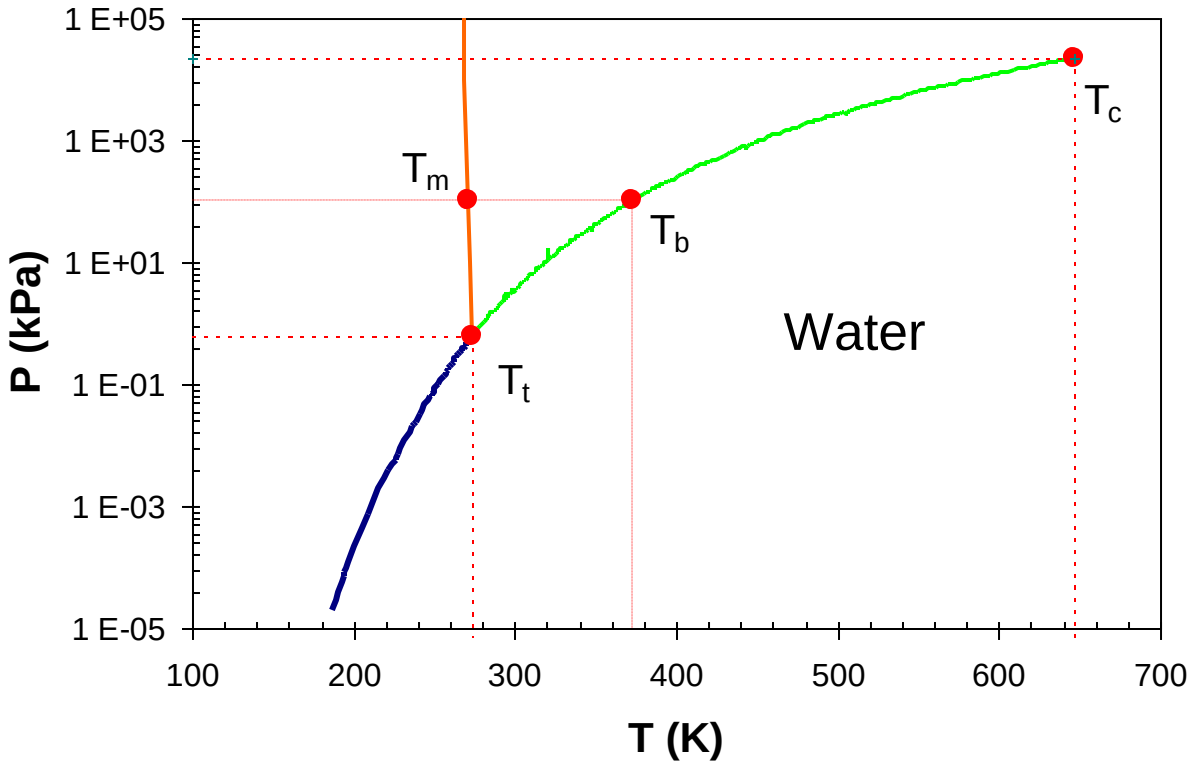
Overview

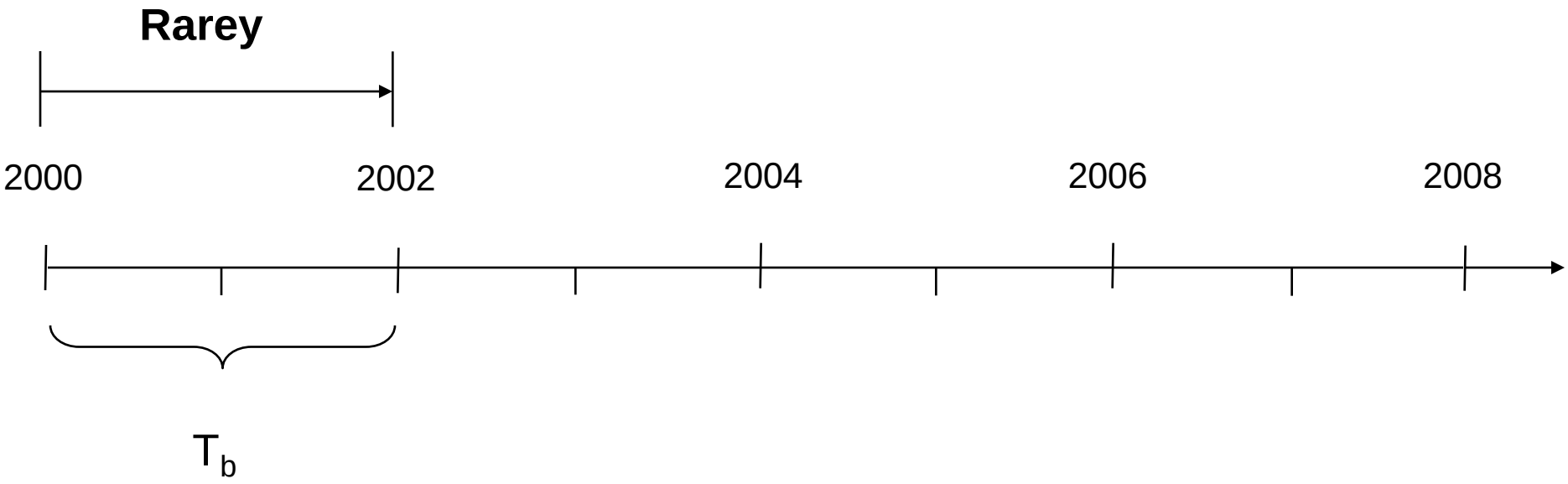
- Motivation
- Project Timeline
- Properties of the Vapor Pressure Curve
- Performance of Different Equations
- Model Description
- Software Tools
- Results
- Future Work
- Acknowledgement

What are Important Properties?

- Usually need to know information about the vapour-liquid boundary, useful for example in:
  - Distillation applications
  - Environmental applications

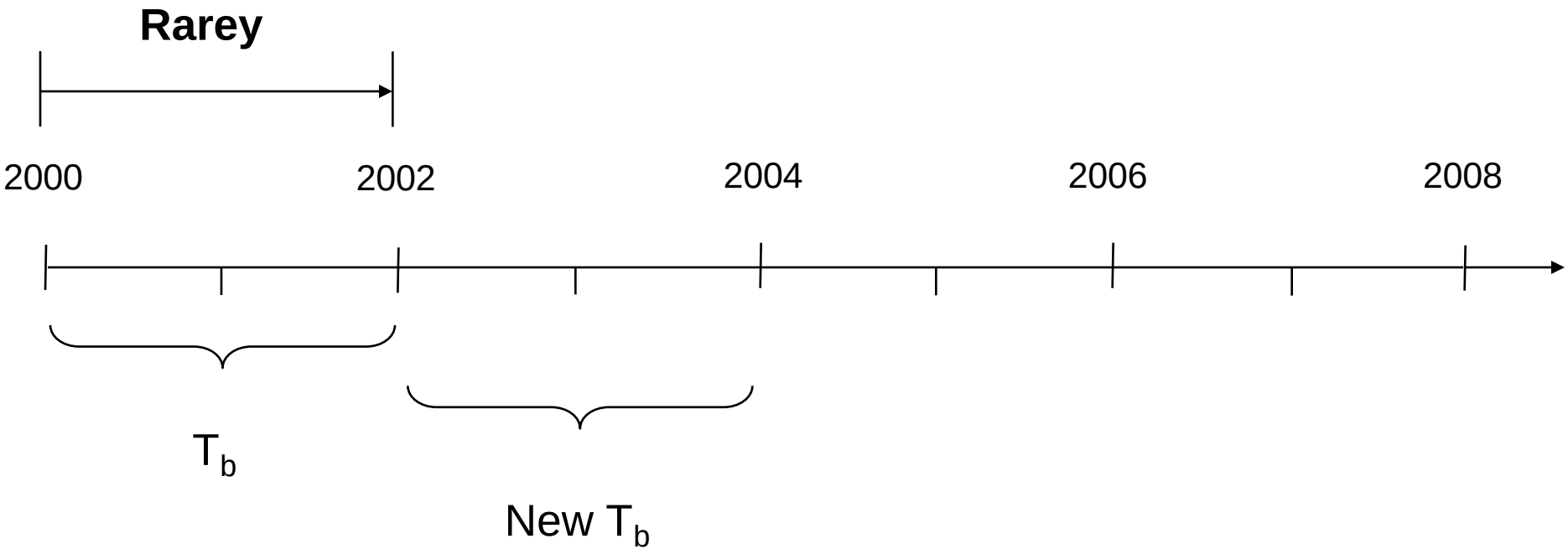


Project Timeline



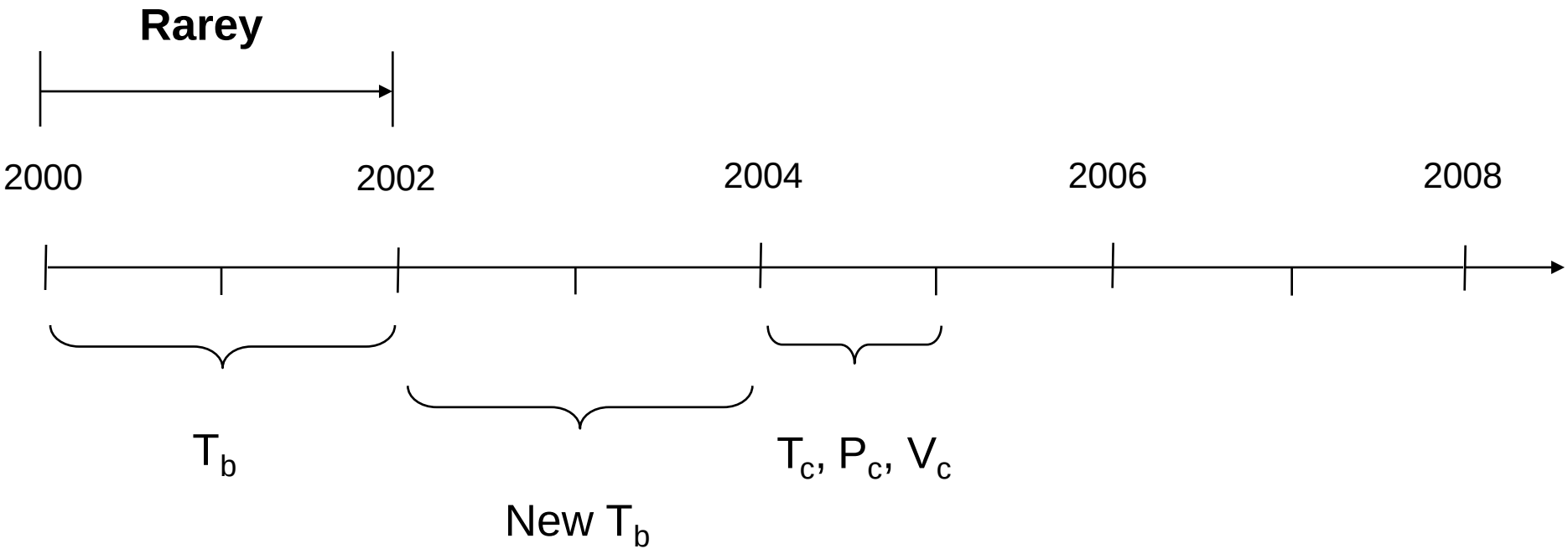
W. Cordes, J. Rarey, *A New Method for the Estimation of the* ***Normal Boiling Point*** *of Non-Electrolyte Organic Compounds*, Fluid Phase Equilibria, 201/2, 397-421 (2002).

Project Timeline



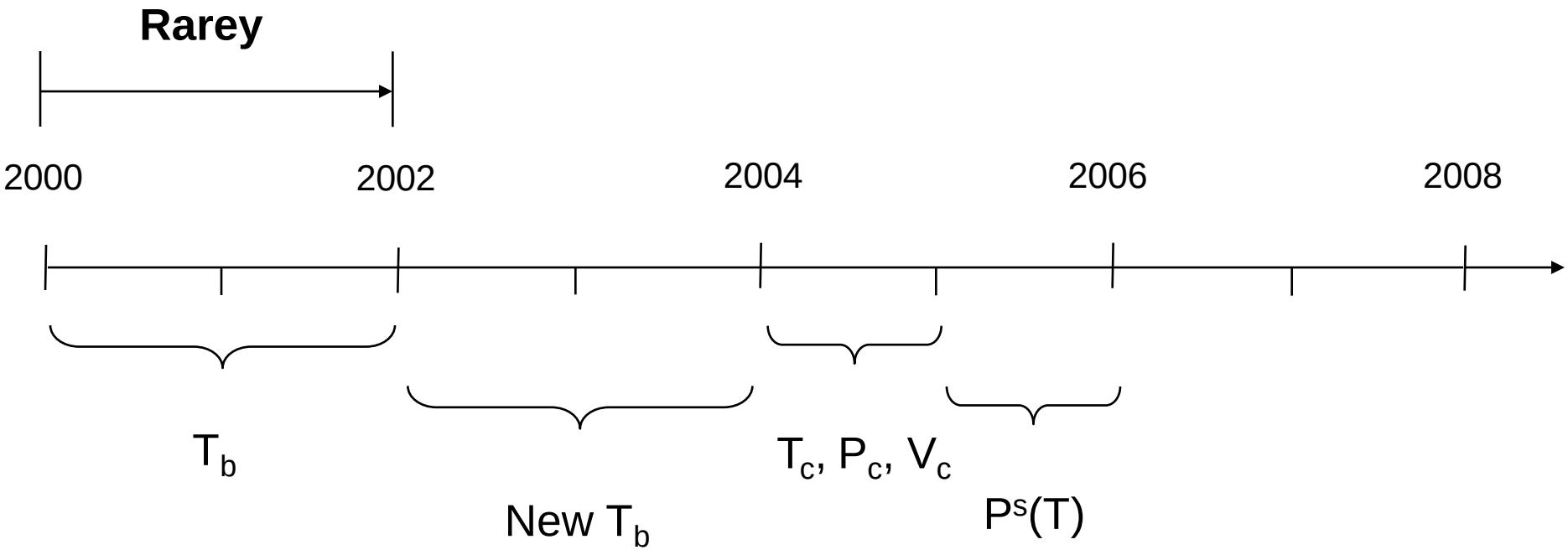
Y. Nannoolal, J. Rarey , D. Ramjugernath, W. Cordes, *Estimation of Pure Component Properties, Part 1: Estimation of the* ***Normal Boiling Point*** *of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions*, Fluid Phase Equilibria, 226, 45-63, 2005.

Project Timeline



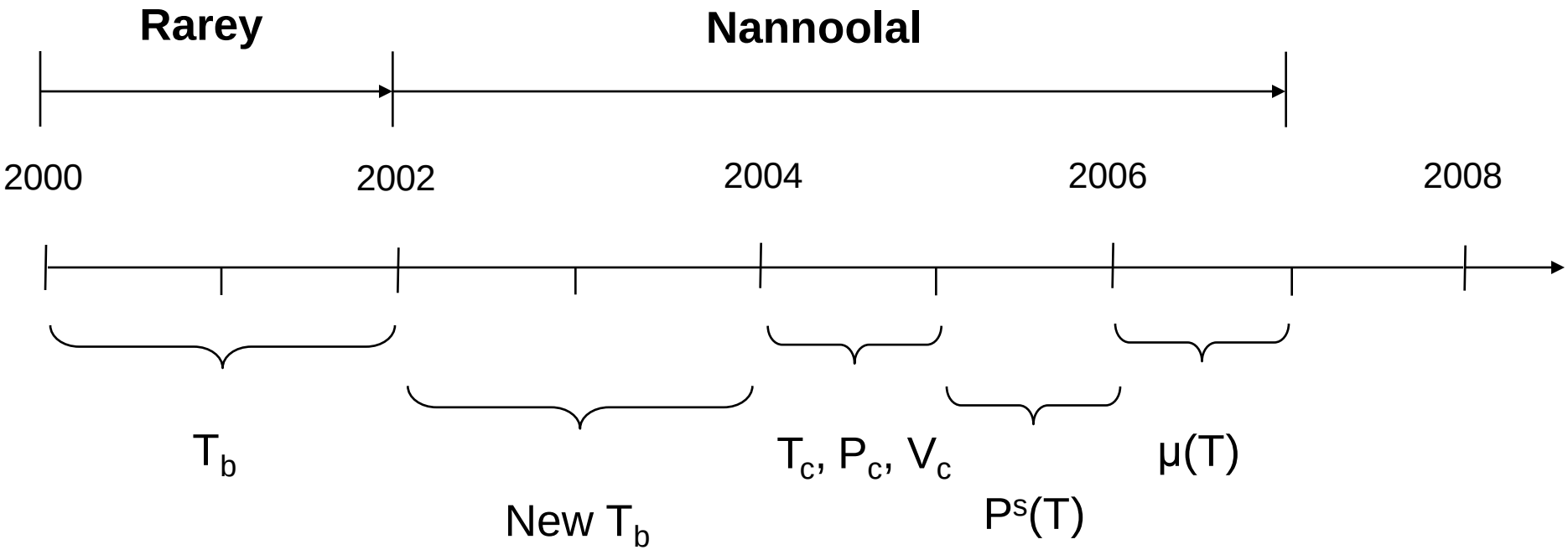
Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 2: Estimation of **Critical Data** by Group Contribution., *Fluid Phase Equilib.*, 252 (2007) 1.

Project Timeline



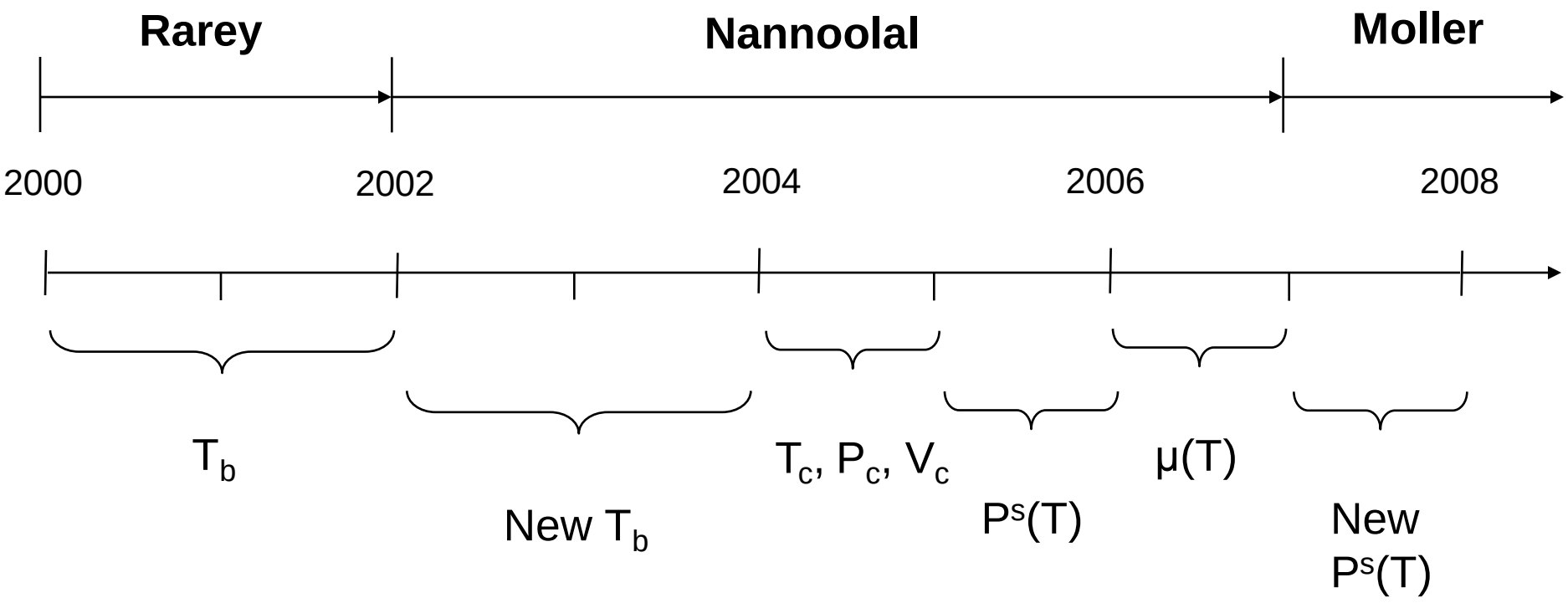
Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 3: Estimation of the **Vapour Pressure** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *Fluid Phase Equilib.* accepted for publication.

Project Timeline



Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 4: Estimation of the **Liquid Viscosity** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *Fluid Phase Equilib.* in preparation.

Project Timeline



Moller, B., Rarey, J., Ramjugernath, D., Estimation of the **Vapour Pressure** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *J. Mol. Liq.* accepted for publication.

Methods for Predicting Physical Properties

- Group contribution methods
  - Fairly simple
  - Good accuracy
  - Need groups to make predictions

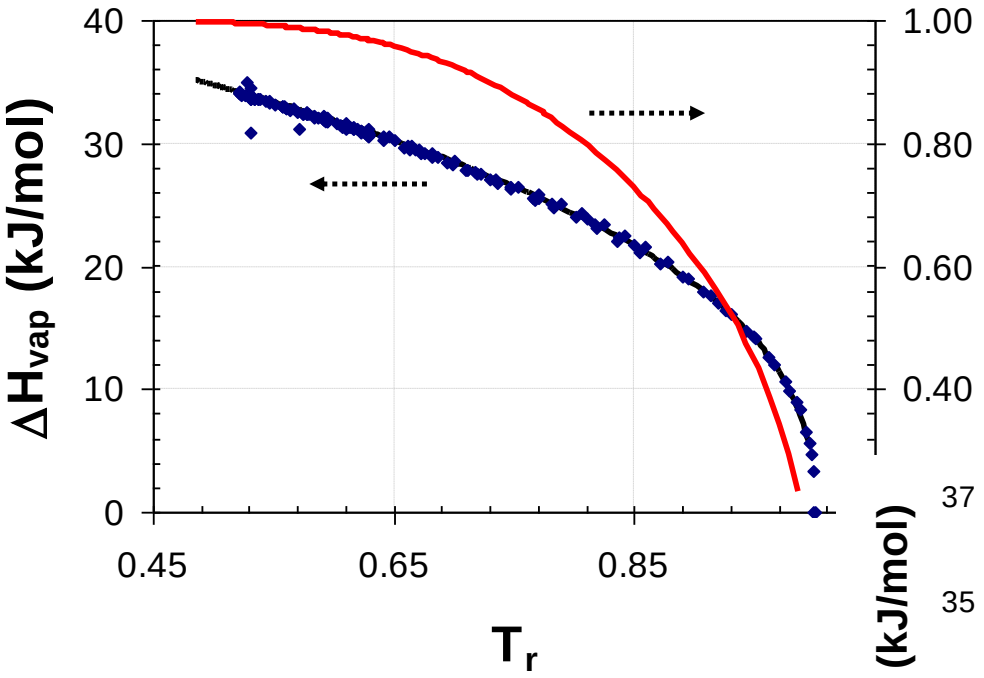
- Quantum chemistry (COSMO-RS, COSMO-SAC …)
  - Great potential but not at the required level of accuracy

- Statistical thermodynamics (molecular simulations …)
  - Can get good results when fitted to some reference data points

Purpose of this Work

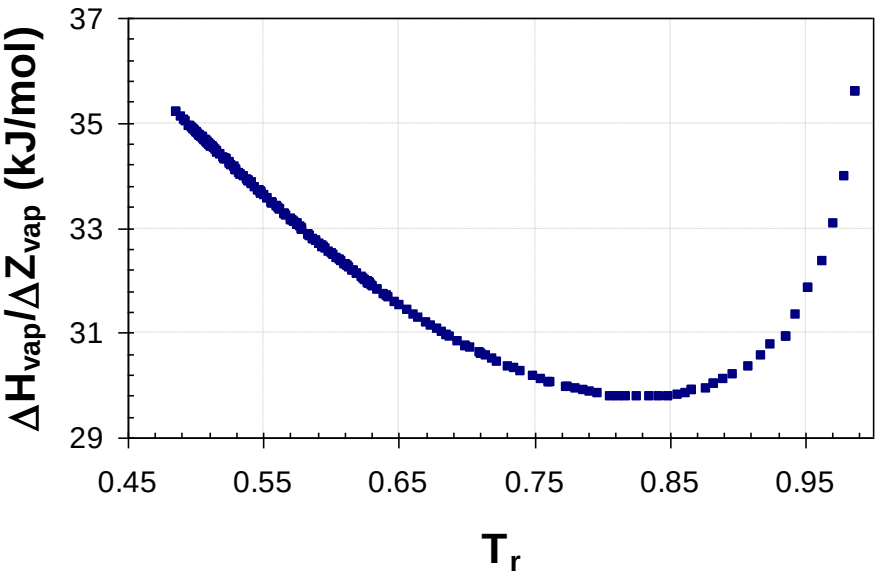
- A large number of good group contribution methods already developed
- Objective of this work was to rework the vapour pressure method
- Nannoolal based his vapour pressure method on the Antoine equation, the first step was therefore to review this decision …

The Slope of the Vapor Pressure Curve

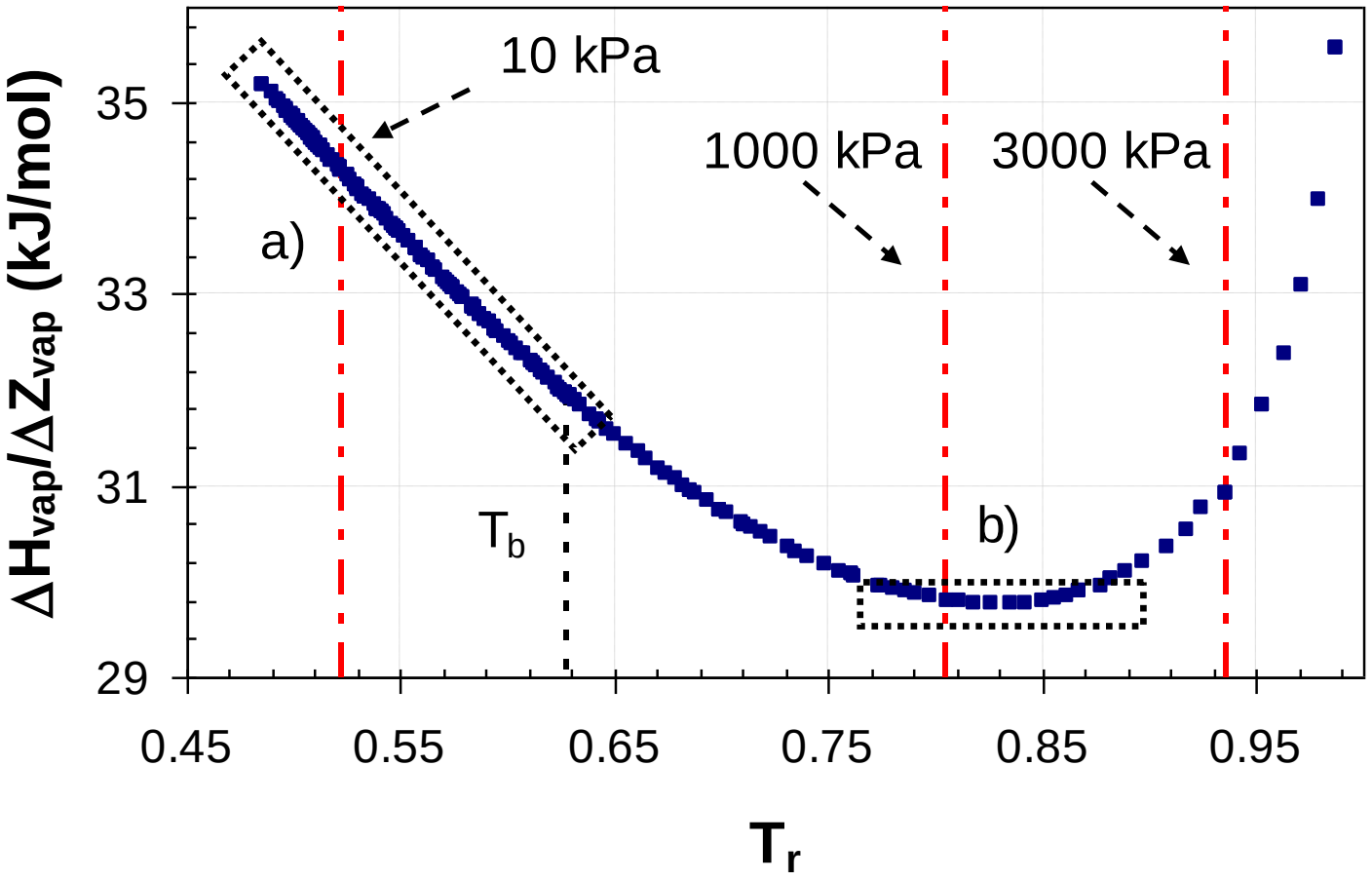


$$\frac{d\ln P^S}{d\left(\frac{1}{T}\right)} = \left(-\frac{1}{R}\right) \times \frac{\Delta H_{vap}}{\Delta Z_{vap}}$$

Component:
Benzene



Approximate Modeling of the Slope



Benzene

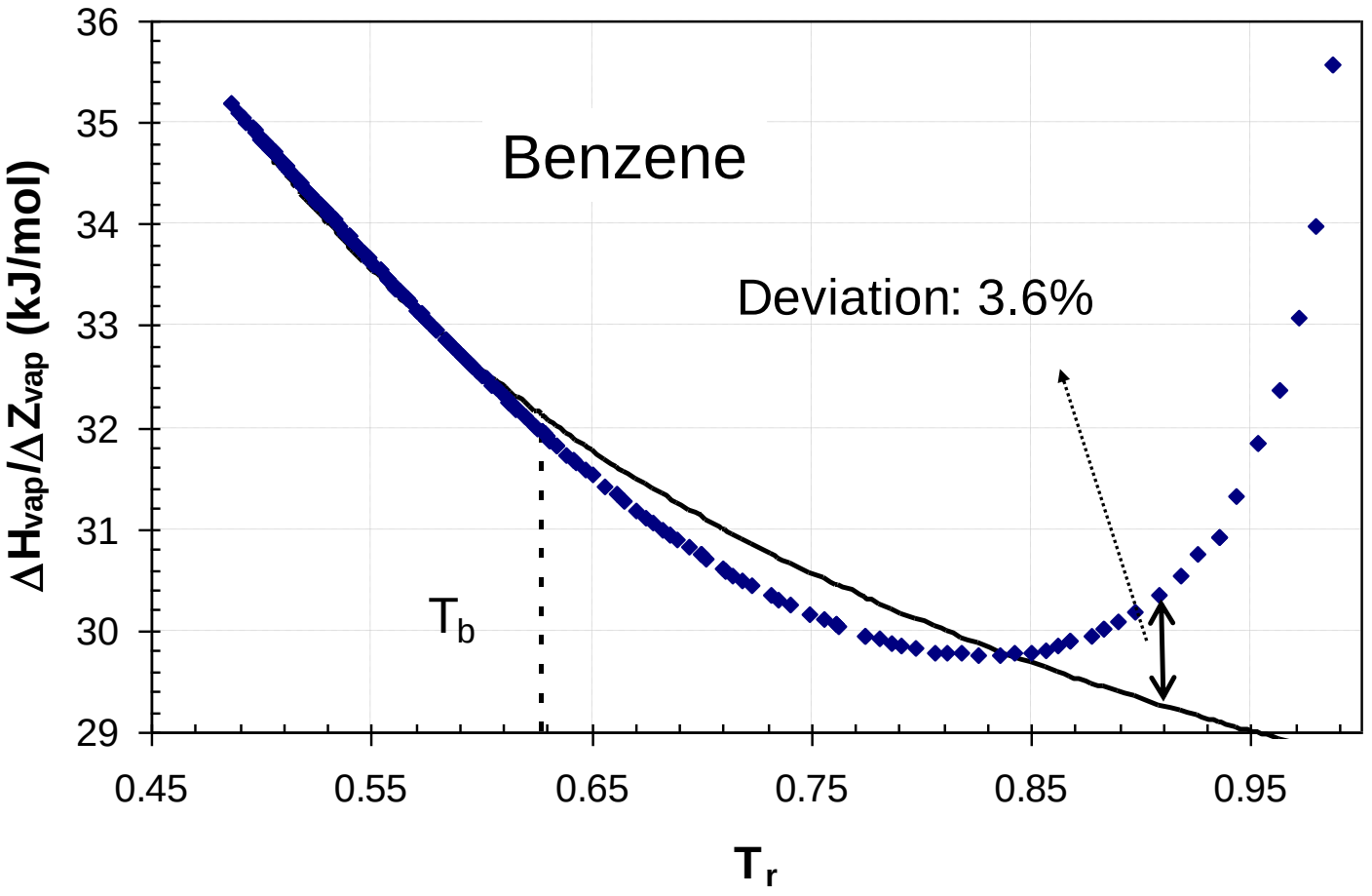
$$\frac{\Delta H_{vap}}{\Delta Z_{vap}}$$

$$T_r = \frac{T}{T_c}$$

a) Linear with respect to: 1/T b) Constant

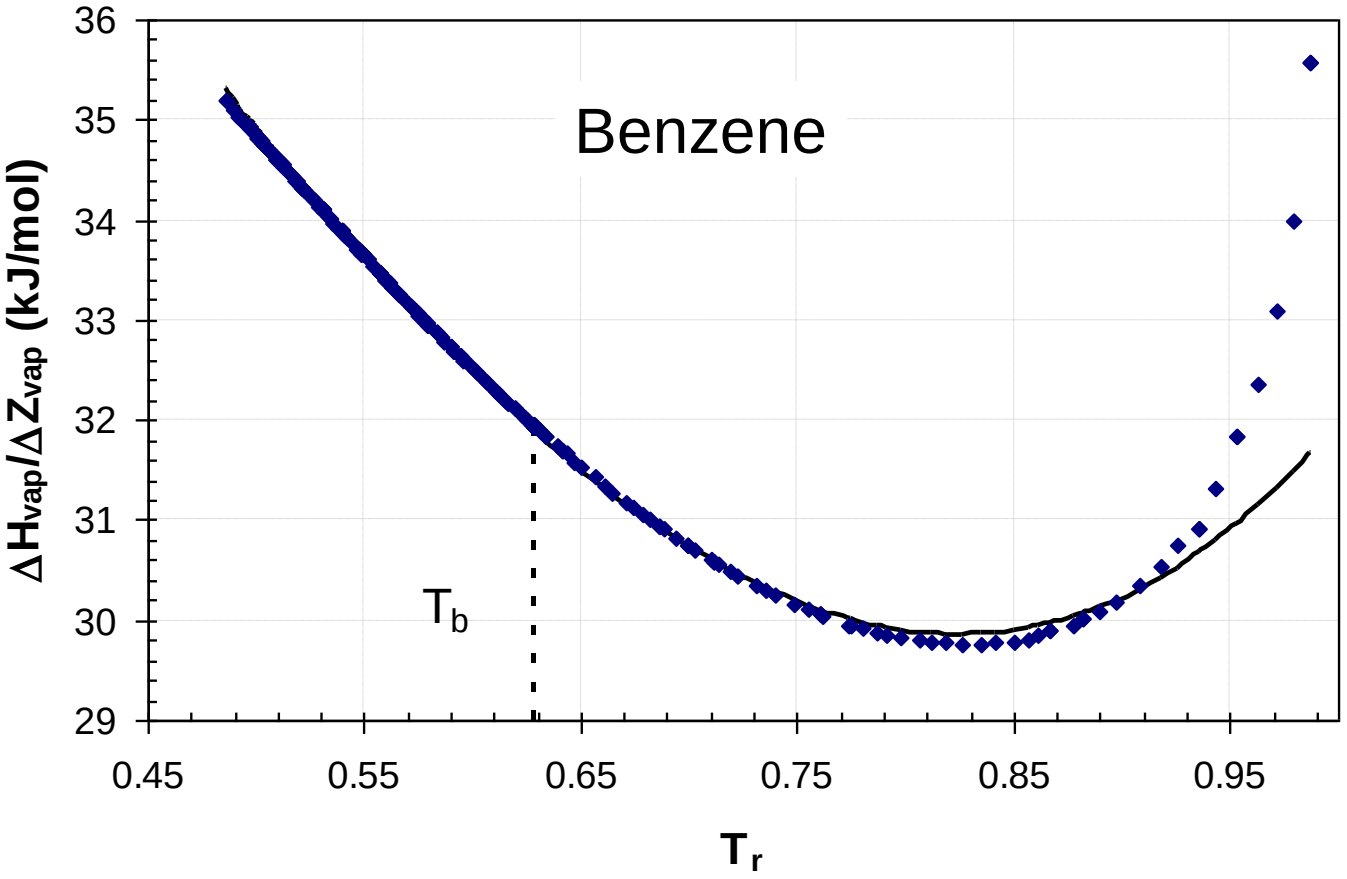
The Antoine Equation

$$\log P^s = A + \frac{B}{T - C}$$



The Cox Equation

$$\log\left(\frac{P^s}{P^{atm}}\right) = A'\left(1-\frac{T_b}{T}\right) \qquad \log A' = \log A_c + E(1-T_r)(F-T_r)$$



$$T_r = \frac{T}{T_c}$$

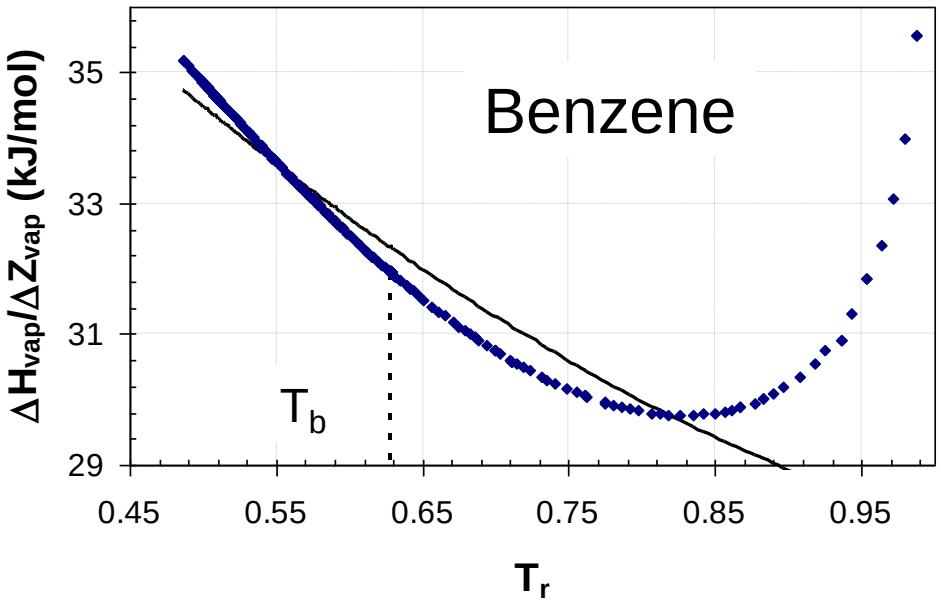
Kinetic Theory of Vaporization

$$\ln P = A + \frac{B}{T} + C\ln T + DT + ET^2$$

$$A = \ln\left(\frac{R}{V_w}\right) + (s-0.5)\ln\left(\frac{E_0}{R}\right) - \ln[\Gamma(s)] + \ln\alpha$$

$$B = -\frac{E_0}{R} \qquad C = 1.5 - s \qquad D = \frac{s-1}{E_0/R}$$

$$E = \frac{2(s-3)(s-1)}{(E_0/R)^2}$$



E_o - Characteristic energy
s - Number of loosely coupled harmonic oscillators

Applicable to pressures lower than ≈200 kPa

Abrams, D. S., Massaldi, H. A., Prausnitz J. M., Vapor Pressures of Liquids as a Function of Temperature. Two-Parameter Equation Based on Kinetic Theory of Fluids., *Ind. Eng. Chem. Fundam.* 13(3) (1974) 259.
Moelwyn-Hughes, E. A., The Chemical Statics and Kinetics of Solutions, Academic Press, London (1971).

Model Derivation

- The A parameter in the Antoine equation is substituted by using the normal boiling point as a reference point:

$$\ln P - \ln P_{atm} = \frac{B}{T - C} - \frac{B}{T_b - C}$$

- In order to further reduce the number of model parameters it is assumed that C is a function of the normal boiling point:

$$\ln\left(\frac{P}{P_{atm}}\right) = B' \frac{T - T_b}{T - C(T_b)}$$

- For aliphatic alcohols and carboxylic acids the new form is:

$$\ln\left(\frac{P}{P_{atm}}\right) = B' \frac{T - T_b}{T - C(T_b)} + D' \ln\left(\frac{T}{T_b}\right)$$

Model Equations

$$\ln\left(\frac{P}{P_{atm}}\right) = B'\frac{T - T_b}{T - C(T_b)} + D'\ln\left(\frac{T}{T_b}\right)$$

(55 GI's)

$$B' = A + dB + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} GI_{i-j}$$

$$C(T_b) = -2.65 + \frac{T_b^{1.485}}{135}$$

Aliphatic alcohols & carboxylic acids

$$D' = D + \frac{1}{n_a}\sum_{i=1}^{m} v_i dE_i$$

(5 Groups)

(158 Groups)

$$dB = \sum_i v_i dB_i + \left(n_a \sum_j v_j dB_j + \sum_k dB_k \right)$$

Frequency

Size

Existence

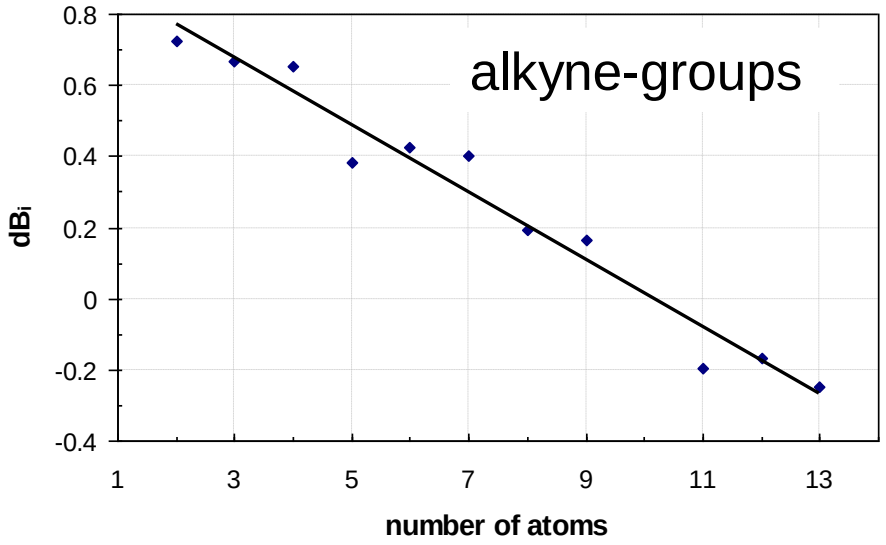
Group interactions (H-bonding groups)

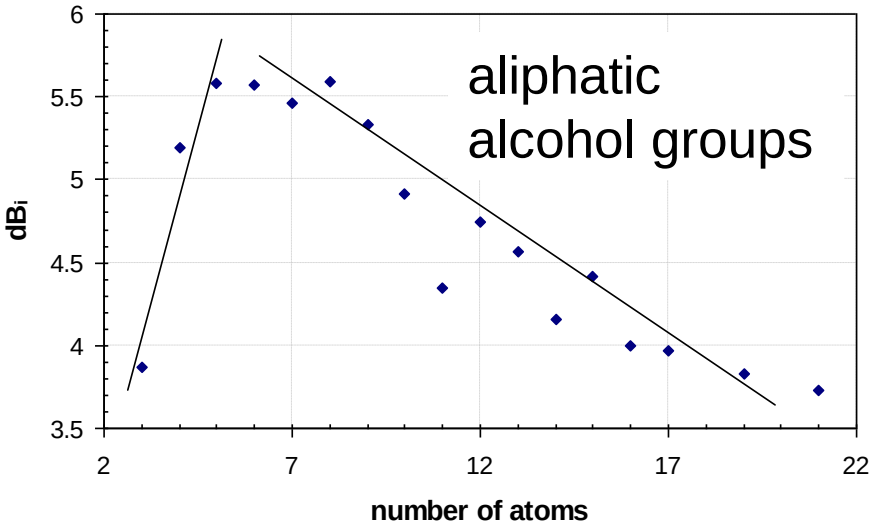
	OH (1)	OH (2)	NH_2
OH (1)	0	1	1
OH (2)	1	0	1
NH_2	1	1	0

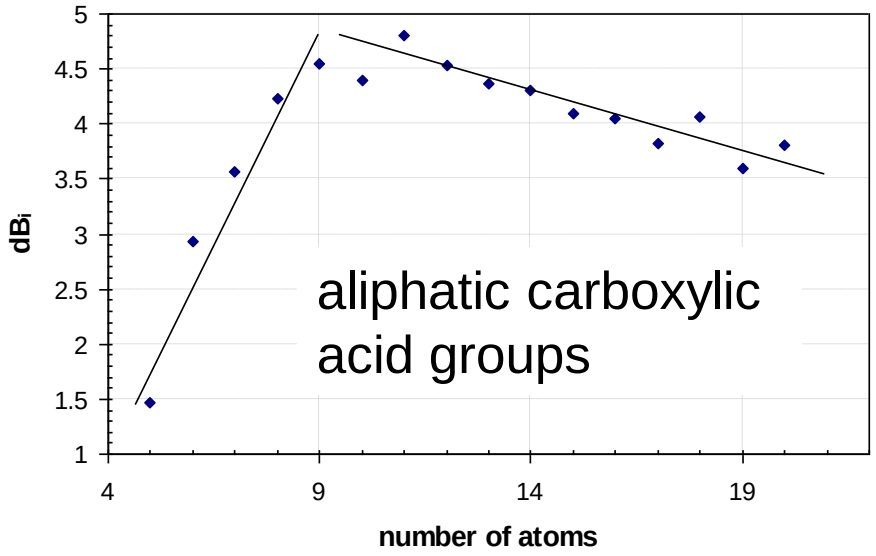
n_a - number of atoms except H

v - frequency of a group

Group Contributions - dB_i as Function of the Number of Heavy Atoms





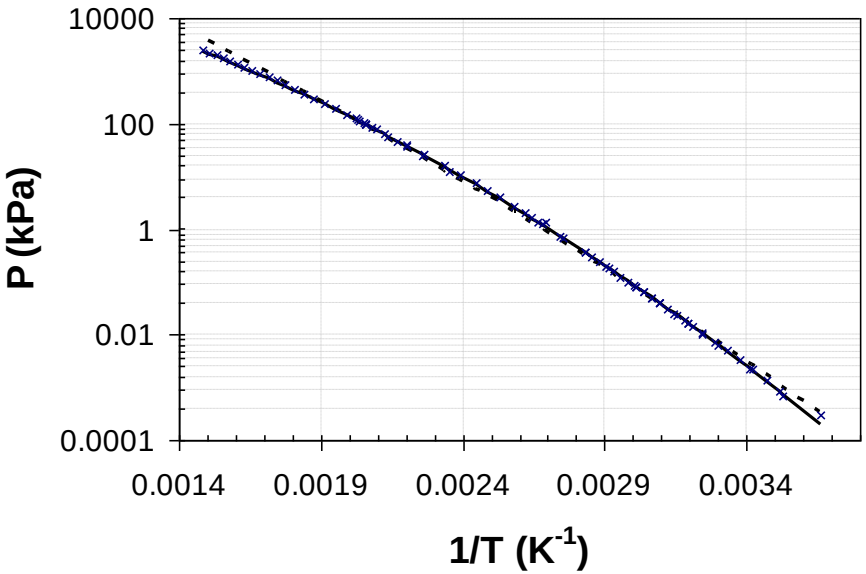


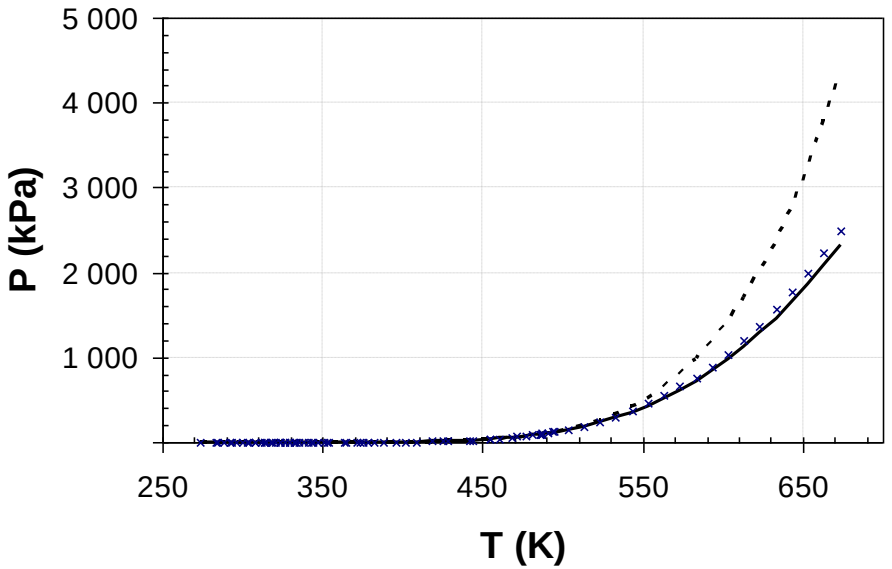
Short and longer chain alcohols and carboxylic acids require separate groups

Model Improvements

- Alcohol and carboxylic acid representation
- Smaller and larger molecules
- Low pressure data

—— Current work
- - - Nannoolal

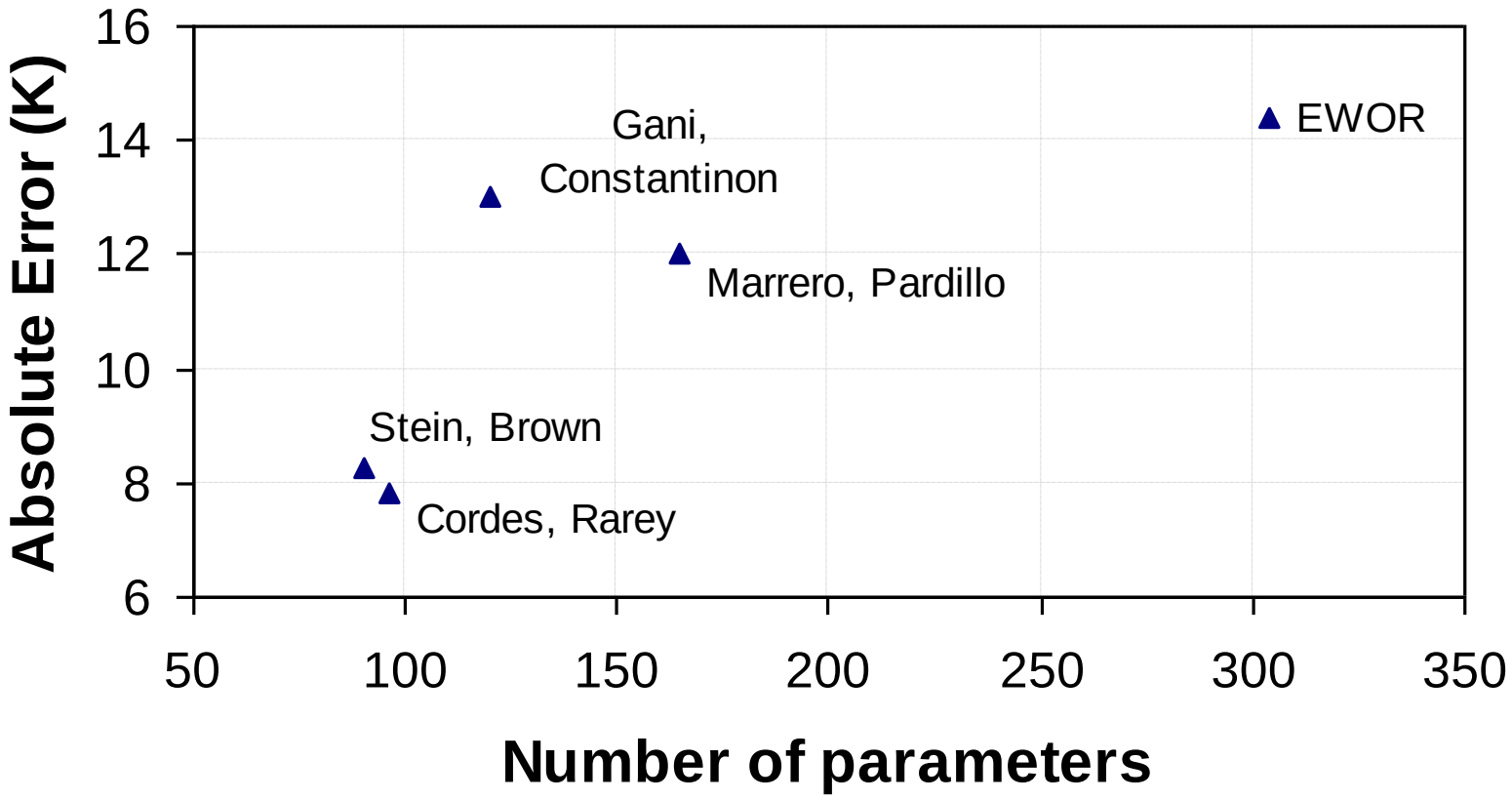




1-Nonanol (data from the DDB)

Model Parameters – Error Relationship

Error for the prediction of the boiling point increases with number of model parameters!



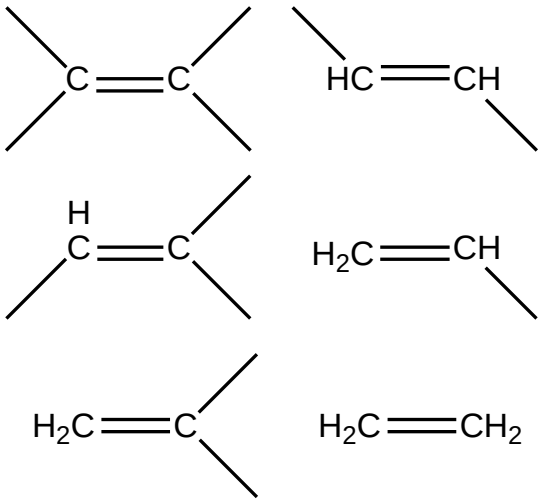
EWOR = Ericksen, Wilding, Oscarson, Rowley

Simplification of Group Definitions

Replace specific groups with more widely applicable groups:

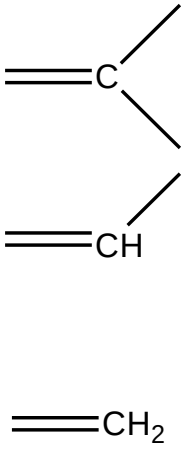
Example: double bonded carbon group:

Previously (Nannoolal et al.)



6 groups to describe all combinations

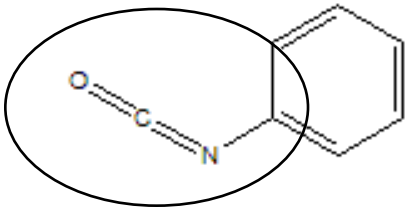
New method



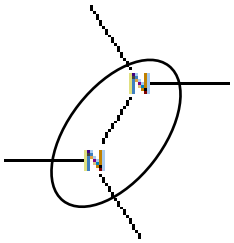
Only 3 groups required to describe all combinations

These simplifications may not be applicable to the estimation of other properties!

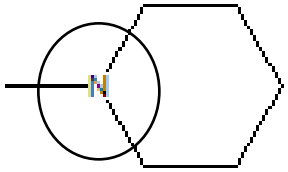
Introduction of New Structural Groups



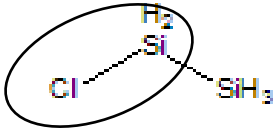
aromatic iso-cyanate



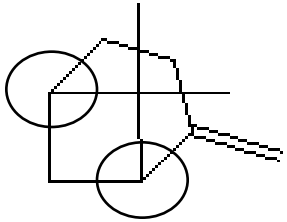
hydrazine



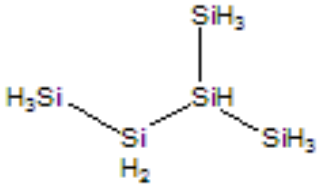
cyclic tertiary amines



halo-silicon groups (F,Cl,Br,I)

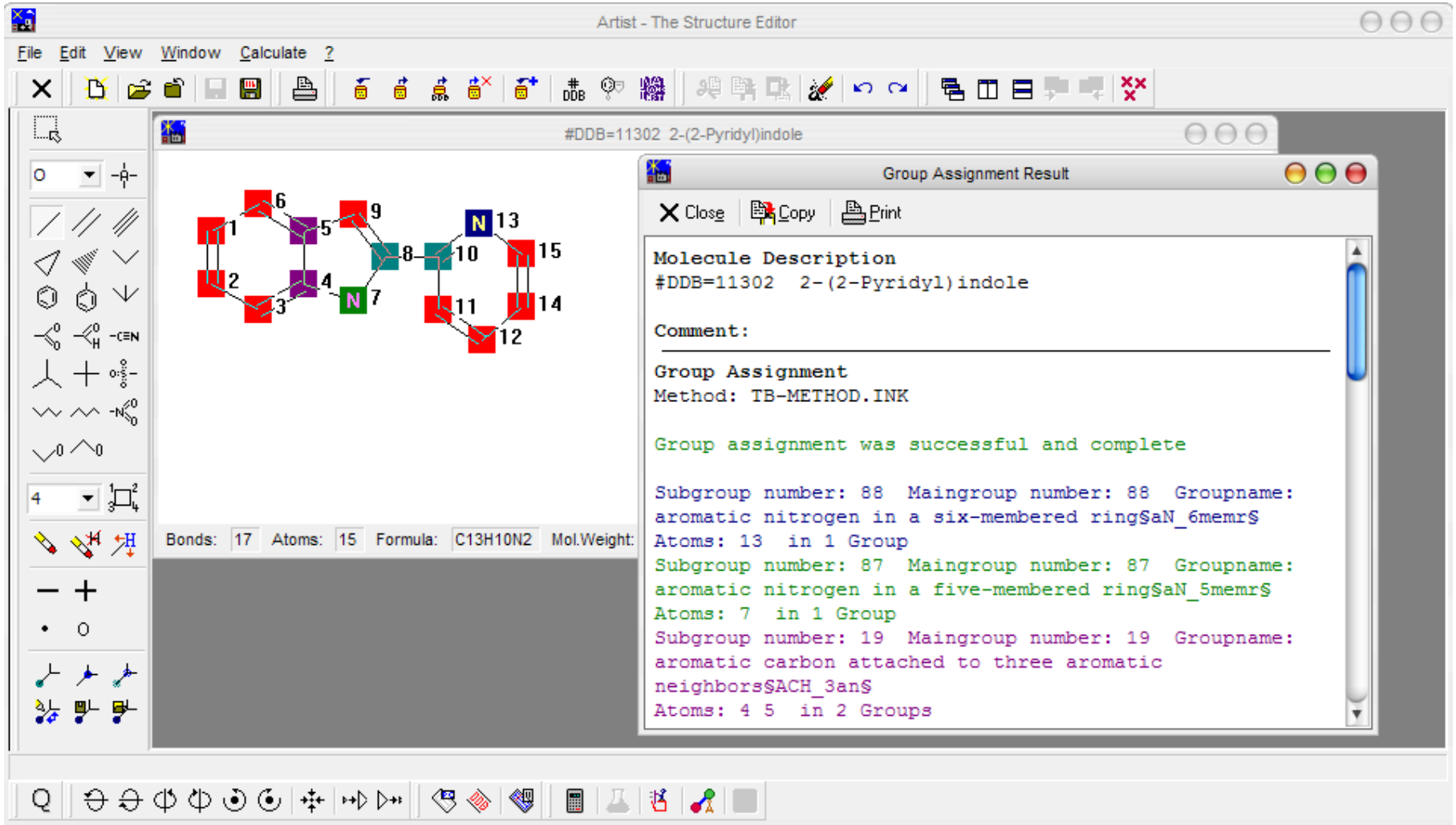


fused ring carbon (and other structural groups)



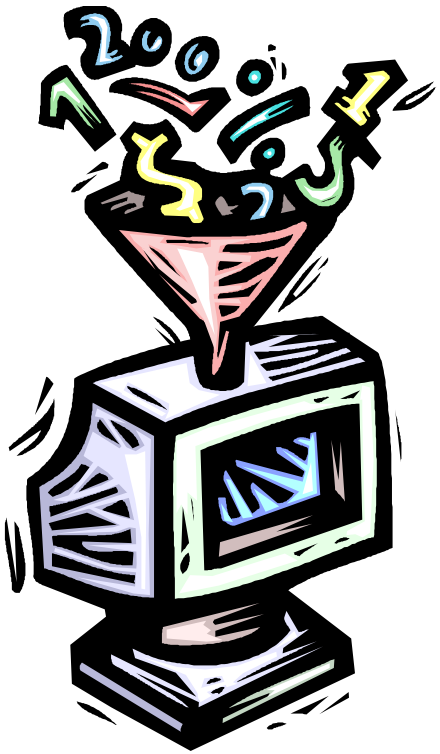
silicon group expanded

Software Tools for Group Analysis

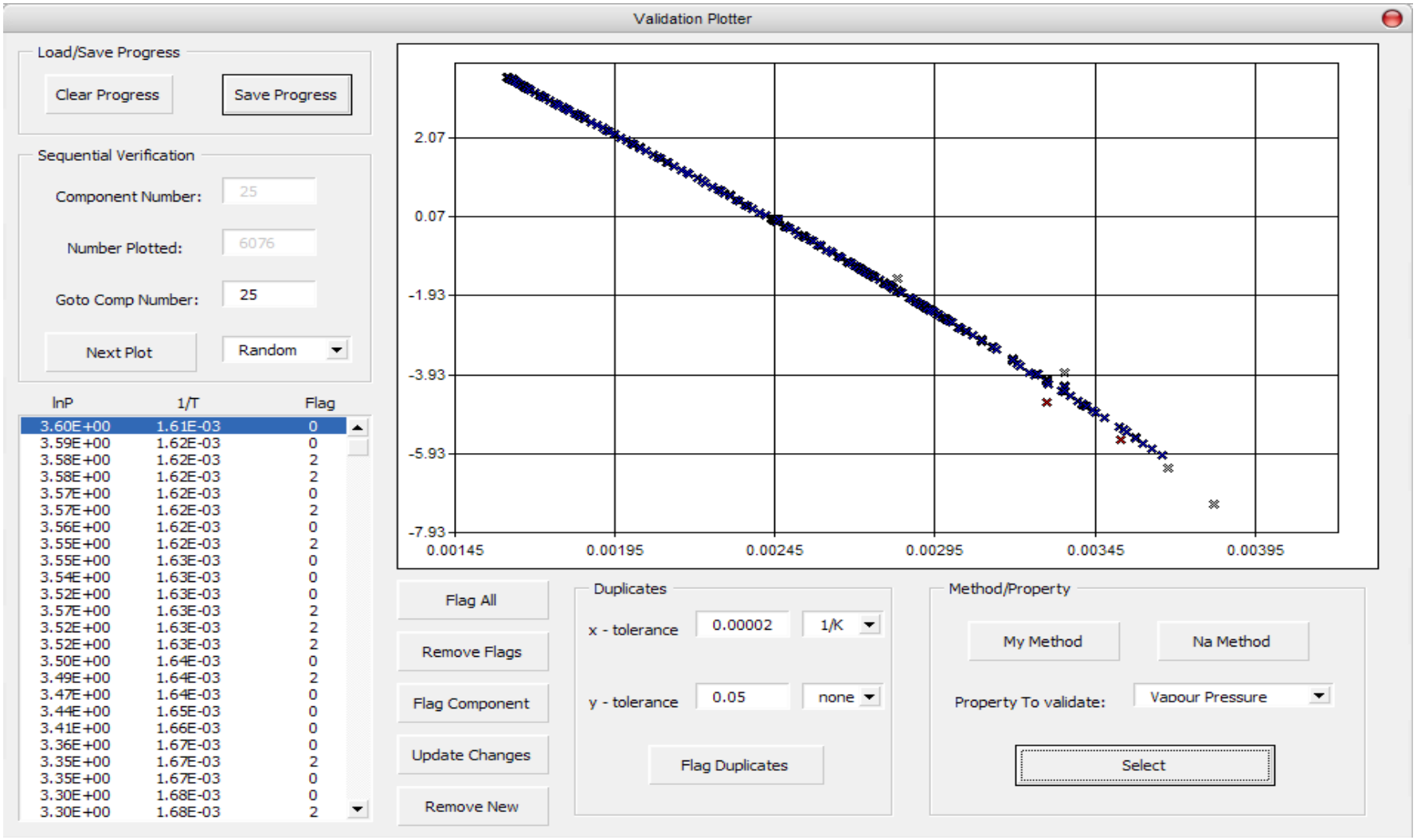


Vapour Pressure Data

- Dortmund Data Bank (DDB)
- VAP data for 6000+ compounds
- 180000+ VAP points
- Data needed to be validated
- Used VBA to streamline the process



Data Validation



Results for All Available Data

Relative mean deviations (%) for the different vapour pressure ranges

$$RMD(\%) = \frac{\left|P^{\exp} - P\right|}{P^{\exp}} \times 100\%$$

	This work (NC = 2332)	Nannoolal et al. (NC = 2207)
Average (All Pressures)	5.0 [113887]	6.6 [111757]
HP (>500 kPa)	5.0 [14678]	5.7 [14310]
MP (10 kPa - 500 kPa)	2.3 [68729]	2.6 [67518]
LP (10 Pa - 10 kPa)	9.8 [28232]	13.1 [27687]
ELP (<10 Pa)	25.7 [2211]	55.2 [2205]

NC – number of compounds

Detailed Results (Relative Mean Deviation (%))

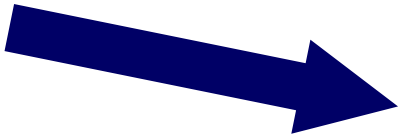
Group	NC	ELP	LP	MP	HP	total
All oxygen compounds	638	27.3 [882]	12.4 [10919]	2.9 [22708]	6.3 [2175]	6.5 [36701]
Carboxylic acids	35	23.9 [116]	12.2 [1823]	3.8 [1106]	13.8 [10]	9.6 [3056]
Aromatic carboxylic acids	1	-	1.6 [111]	2.7 [22]	-	1.8 [133]
Aliphatic carboxylic acids	34	23.9 [116]	12.8 [1712]	3.8 [1084]	13.8 [10]	9.9 [2923]
Alcohols	167	28.3 [312]	17.2 [3761]	4.1 [7186]	10.8 [626]	9.2 [11886]
Aromatic alcohols	55	39.9 [26]	25.1 [678]	3.1 [1277]	6.9 [69]	11.0 [2050]
Aliphatic alcohols	112	27.3 [286]	15.5 [3083]	4.3 [5909]	11.3 [557]	8.8 [9836]
Ethers	92	23.7 [17]	6.5 [771]	1.8 [3743]	3.4 [738]	2.8 [5269]
Esters	158	29.0 [326]	8.4 [2445]	2.2 [5622]	5.6 [403]	5.1 [8809]
Ketones	64	19.0 [75]	8.9 [886]	1.9 [2637]	4.4 [271]	4.0 [3869]
Aldehydes	30	6.1 [4]	12.1 [393]	2.4 [736]	5.1 [19]	5.7 [1153]
Carbonate diesters	3	-	1.8 [30]	0.8 [289]	-	0.9 [319]
Anhydrides	6	-	14.9 [54]	4.4 [81]	-	8.6 [135]
Epoxides	11	-	2.9 [33]	1.8 [280]	2.3 [43]	1.9 [356]
Carbonates	3	38.7 [3]	9.1 [150]	3.2 [92]	4.4 [10]	7.2 [255]
Ureas	5	14.8 [3]	10.5 [59]	2.2 [40]	-	7.4 [102]

NC – number of compounds
ELP – extremely low pressure P < 10 Pa
LP – low pressure 10 Pa < P < 10 kPa
MP – medium pressure 10 kPa < P < 500 kPa
HP – high pressure P > 500 kPa
total – whole vapour pressure range

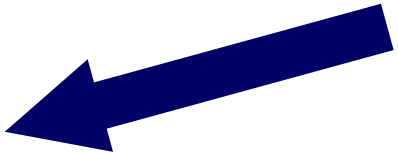
Quality Analysis

- Can use the error tables to give an approximate quality of prediction:

Compound to be predicted

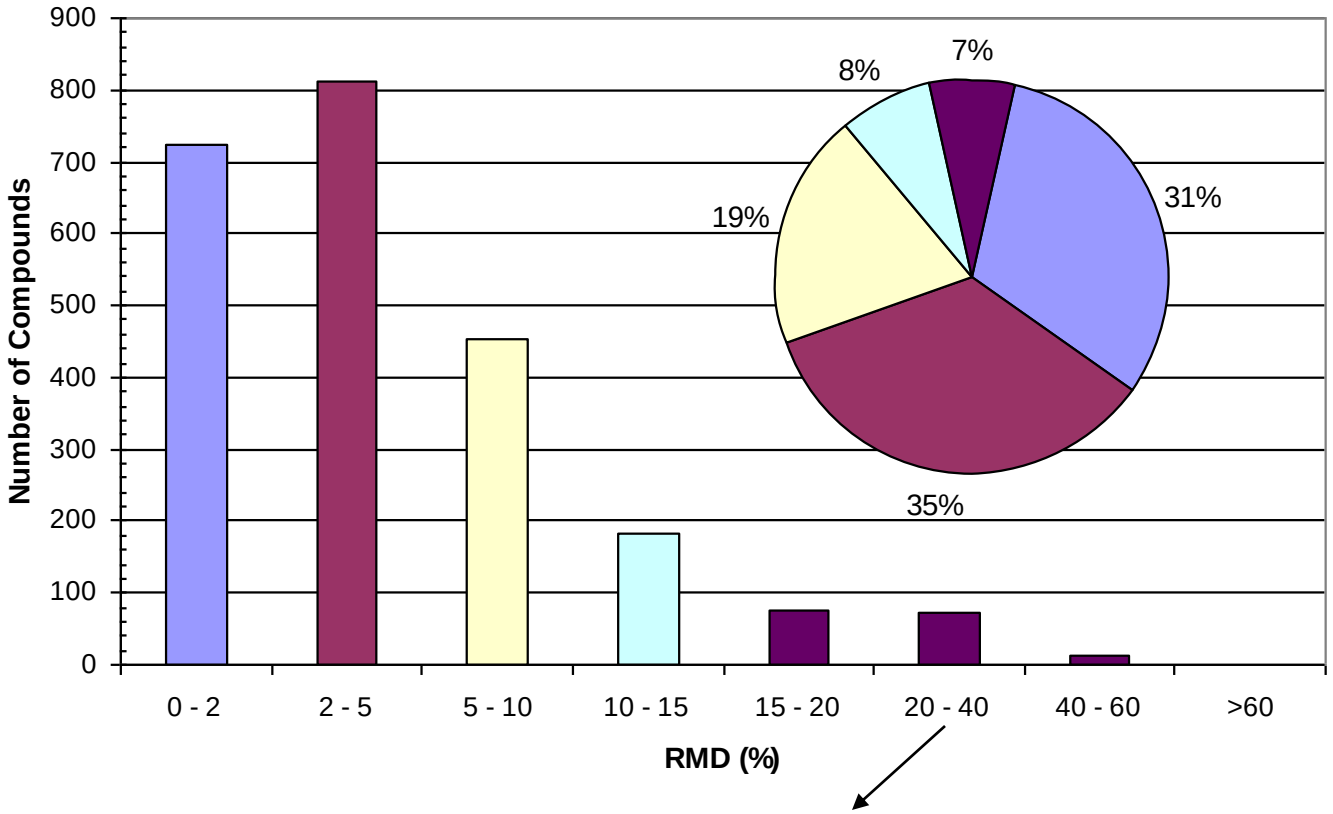


Select most specific group which the compound falls into (e.g. n-alcohols)



Give quality analysis based on training set errors

RMD(%) Histogram for the Data in the Training Set



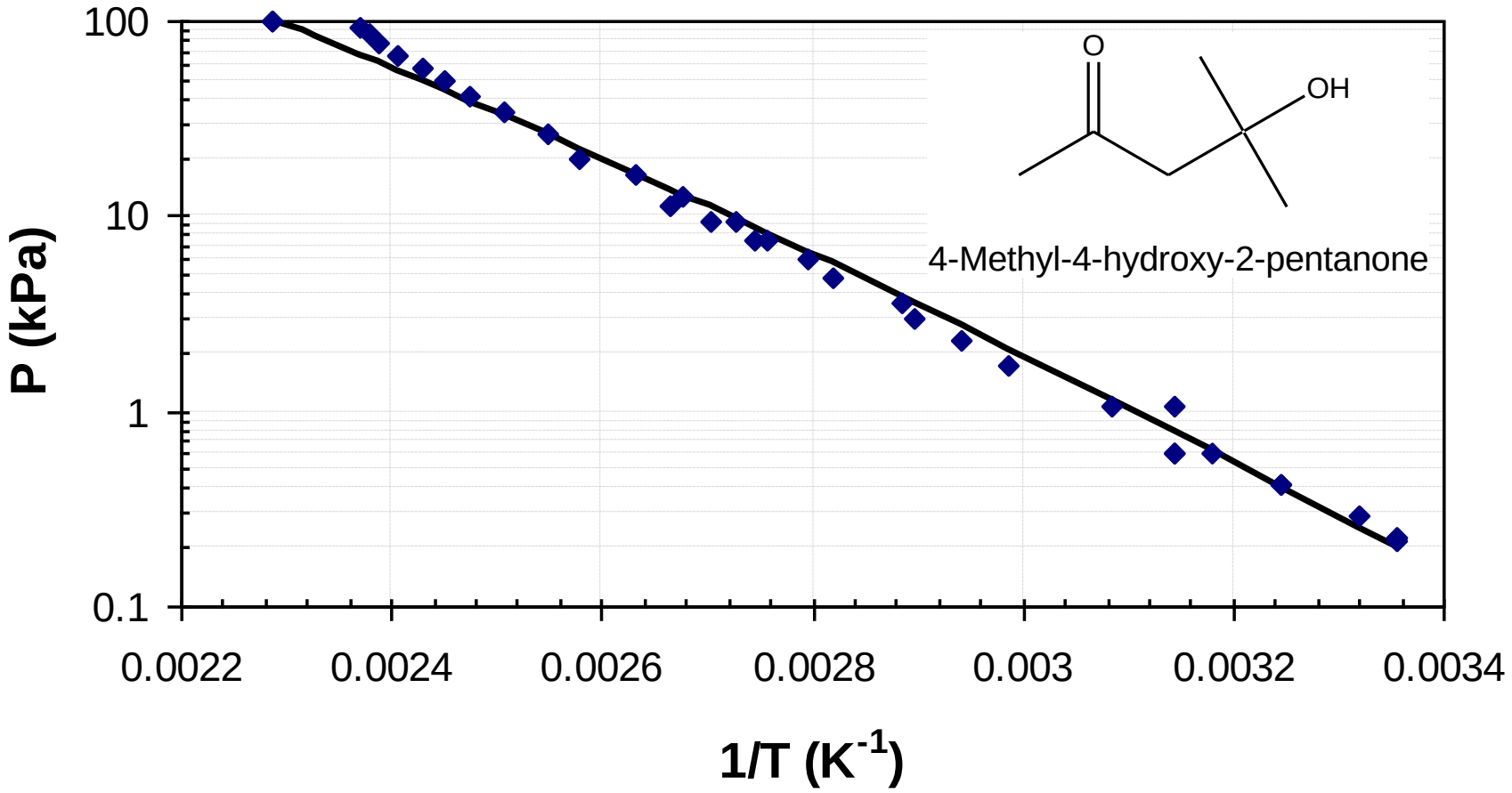
Typically compounds with large amounts of low vapour pressure data for example squalane (C30H62)

Results for a Test Set not Used in the Regression

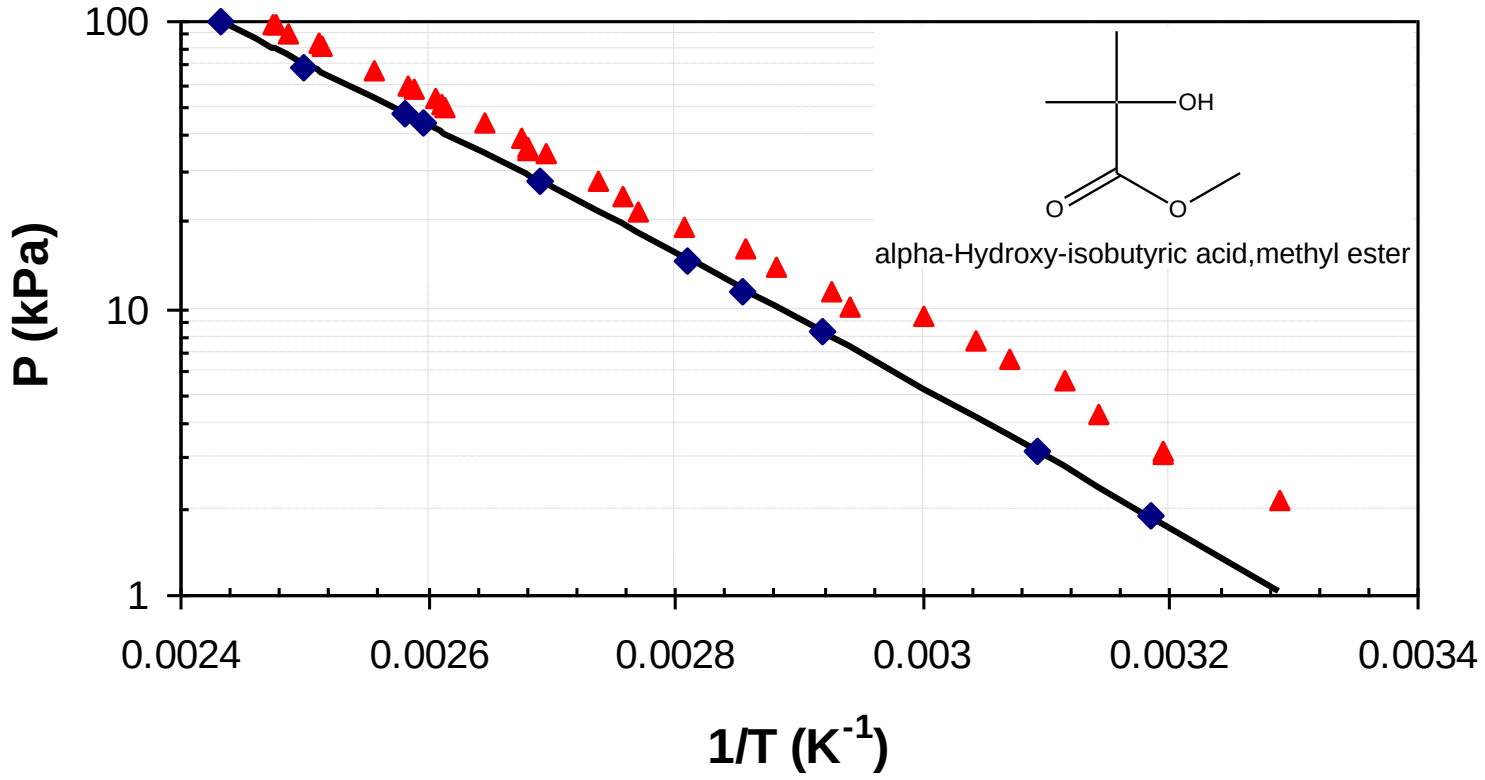
	New Method		Nannoolal et al.	
Compound Class	**NC**	**RMD%**	**NC**	**RMD%**
Hydrocarbons	59	6.5 [486]	59	7.5 [486]
Halogen compounds	14	7.0 [73]	14	7.1 [73]
Oxygen compounds	46	7.1 [1952]	44	8.5 [1938]
Nitrogen compounds	19	7.3 [172]	18	8.9 [169]
Sulfur compounds	3	5.6 [24]	3	11.0 [24]
All compounds	157	7.1 [2879]	154	8.2 [2859]

Test set contains data with higher scatter or where the reliability could not be verified (only one author, …)

Specific Test Set Examples



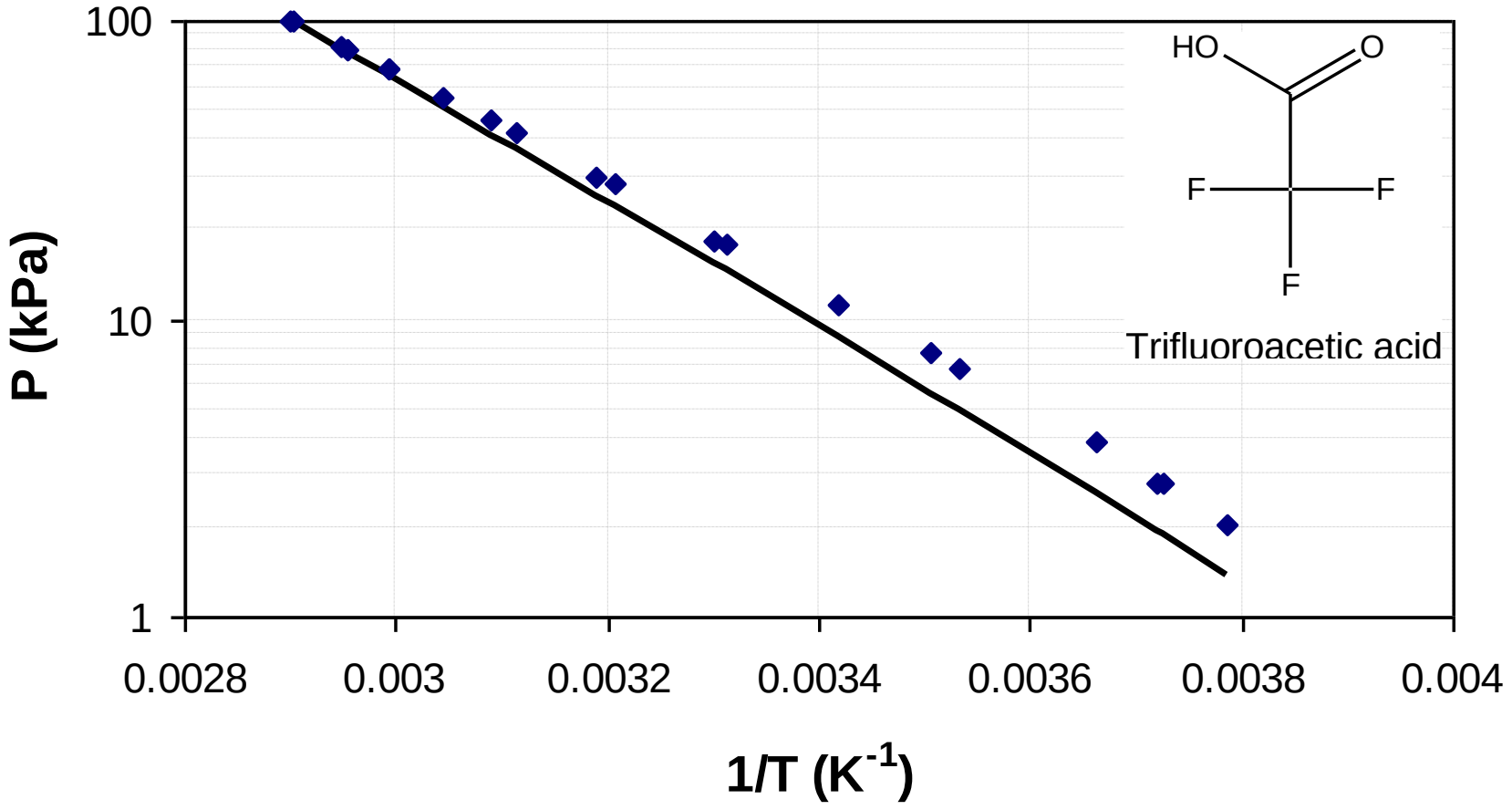
Specific Test Set Examples



♦ Danov S.M., Obmelyukhina T.N., Chubarov G.A., Balashov A.L., Dolgopolov A.A., J.Appl.Chem.USSR, 63(3), 566-568, 1990

▲ Matin N.B., Khitrin S.V., Spasskaya R.I., Trachenko V.I., Zilberman E.N., Soluyanova T.F., Zh.Prikl.Khim.(Leningrad), 53(9), 1999-2003, 1980

Specific Test Set Examples



Heat of Vaporization at 298.15 K

$$\Delta H_{vap} = -R\Delta Z_{vap}\left[B'\frac{(C(T_b)-T_b)}{\left(1-\frac{C(T_b)}{T}\right)^2}-D'T\right]$$

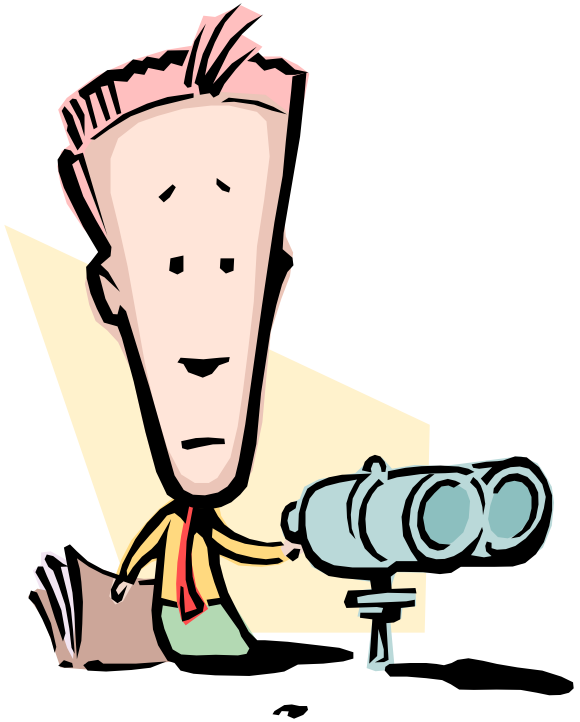
	This Work		Kolská et al.*	
Compound Class	**NC**	**RMD(%)**	**NC**	**RMD(%)**
Hydrocarbons	197	2.9	236	2.0
Halogen Compounds	89	2.1	103	2.0
Oxygen Compounds	224	4.2	262	2.3
Nitrogen Compounds	101	2.9	104	2.4
Phosphorous Compounds	1	6.9	-	-
Sulphur Compounds	38	2.6	52	2.2
Metals	4	5.6	-	-
Other Compounds	1	7.4	-	-
Silicon Compounds	12	9.2	11	3.1
All Compounds	718	3.5	831	2.2

*Kolská Z., Růžička V., Gani R., Ind. Eng. Chem. Res., 44, 8436-8454, 2005

Future Work

- Prediction of further properties
  - Ground work has been done
  - Overlap project so there is a transfer of knowledge

- Prediction of mixture properties



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