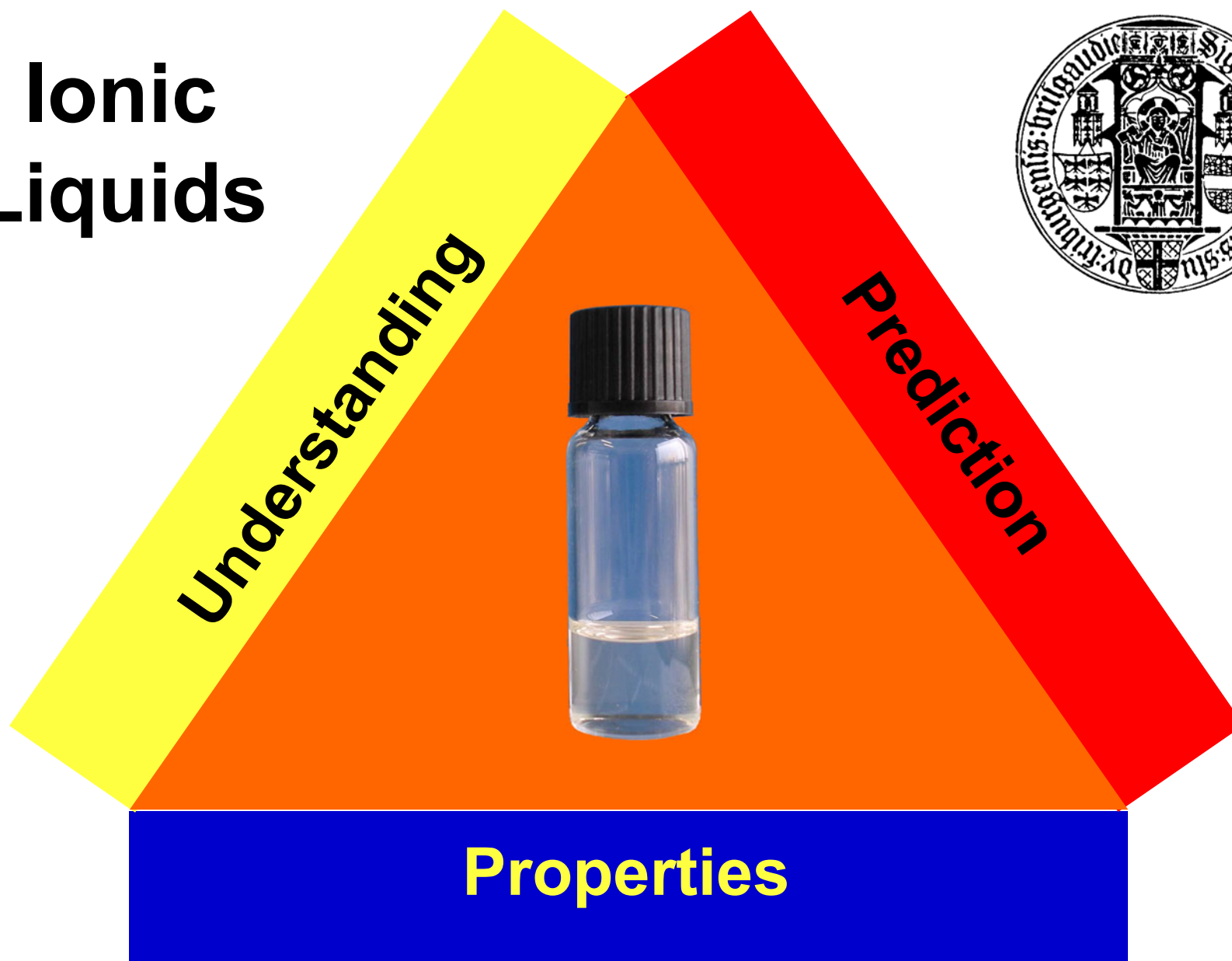


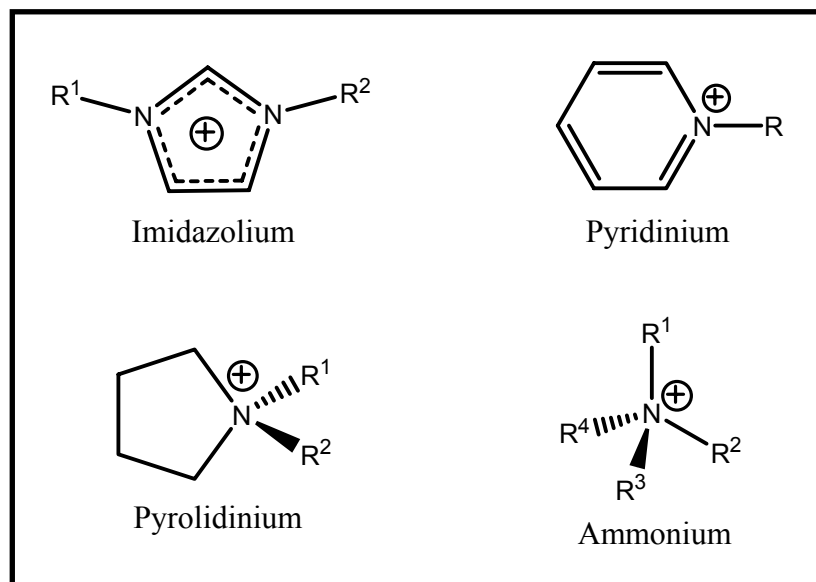
Ionic Liquids



Ingo Krossing*, Albert-Ludwigs-Universität Freiburg.
C. Daguenet, P. Dyson, A. Oleinikova, T. Schubert,
J.M. Slattery, S. Bulut, H. Weingärtner.

What are ionic liquids?

- Generally defined as salts which melt below 100 °C
- Often composed of a large organic cation and a complex anion e.g. $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{O}_3\text{SCF}_3]^-$, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$



- It has been estimated that there may be 10^{12} - 10^{18} ILs!

- => It is almost impossible to prepare all likely combinations.
- => Usually one has restraints on using a new IL (m.p., conductivities, viscosities, densities, polarities etc.).
- => Is it possible to understand and predict quantitatively the physical properties of ionic liquids...?**

Recent review on semi-empirical methods for the prediction of physical properties of ILs:

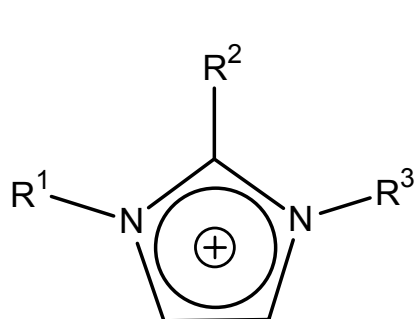
I. Krossing, J. Slattery, Z. Physik. Chem. **2006**, in press.

Melting Point Predictions

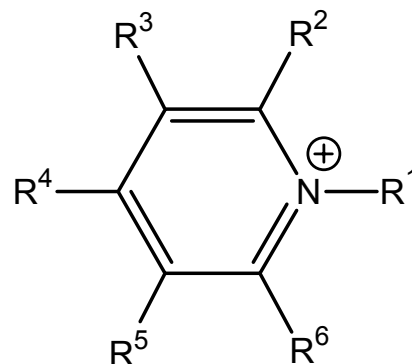
- Quantitative Structure-Property Relationship (QSAR) methods
 - Large trainingsets with accurate experimental data of related ILs needed.
 - Physical properties of related ILs may then be predicted.
 - CODESSA-code often used.^[1]

^[1] A.R. Katritzky, V. S. Lobanov, M.Karelson; CODESSA, University of Florida **1994**.

Quantitative Structure-Property Relationship (QSAR) Methods^[1]



Imidazolium

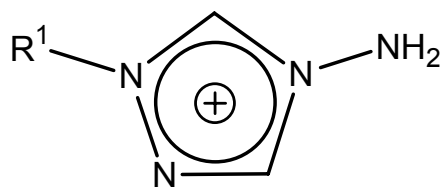


Pyridinium

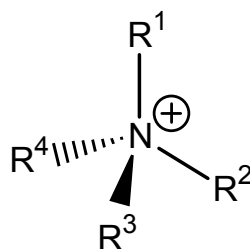
- r^2 between 0.7 and 0.94
- Best dataset (imidazolium bromides; $r^2 = 0.94$):

$$s_{est} = 24 \text{ K}$$

=> Qualitative trends good.



4-amino-1,2,4-triazolium



Ammonium

^[1] a) Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. J. Chem. Inf. Comput. Sci. 2002, 42, 225-231; b) Katritzky, A. R.; Lomaka, A.; Petrukhin, R.; Jain, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. J. Chem. Inf. Comput. Sci. **2002**, 42, 71-74; c) Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Karelson, M.; Visser, A. E.; Rogers, R. D. J. Chem. Inf. Comput. Sci. **2005**, 45, 533-534.

Molecular Dynamics Simulations^[1]

- Force fields optimized for ILs.
 - Previously existing force fields with some modification.
- => Valuable insights into the structure, dynamics and solvent properties of ILs.
- => Calculate temperature and pressure dependent densities, molar volumes, volume expansivities and isothermal compressibilities of ILs.

^[1] e.g. Alavi, S.; Thompson, D. L. J. Chem. Phys. **2005**, 122, 154704-154712.

Molecular Dynamics Simulations^[1]

- => Difficult to define melting point (m.p.)...
- => Only one study addresses m.p.:^[1]



- => Diffusion of P-atom used as indicator.
- => Exp. m.p.: 332 K; predicted m.p.: 375 K.
- => Crystal structure needed as starting point.

^[1] e.g. Alavi, S.; Thompson, D. L. J. Chem. Phys. **2005**, 122, 154704-154712.

A thermodynamic approach

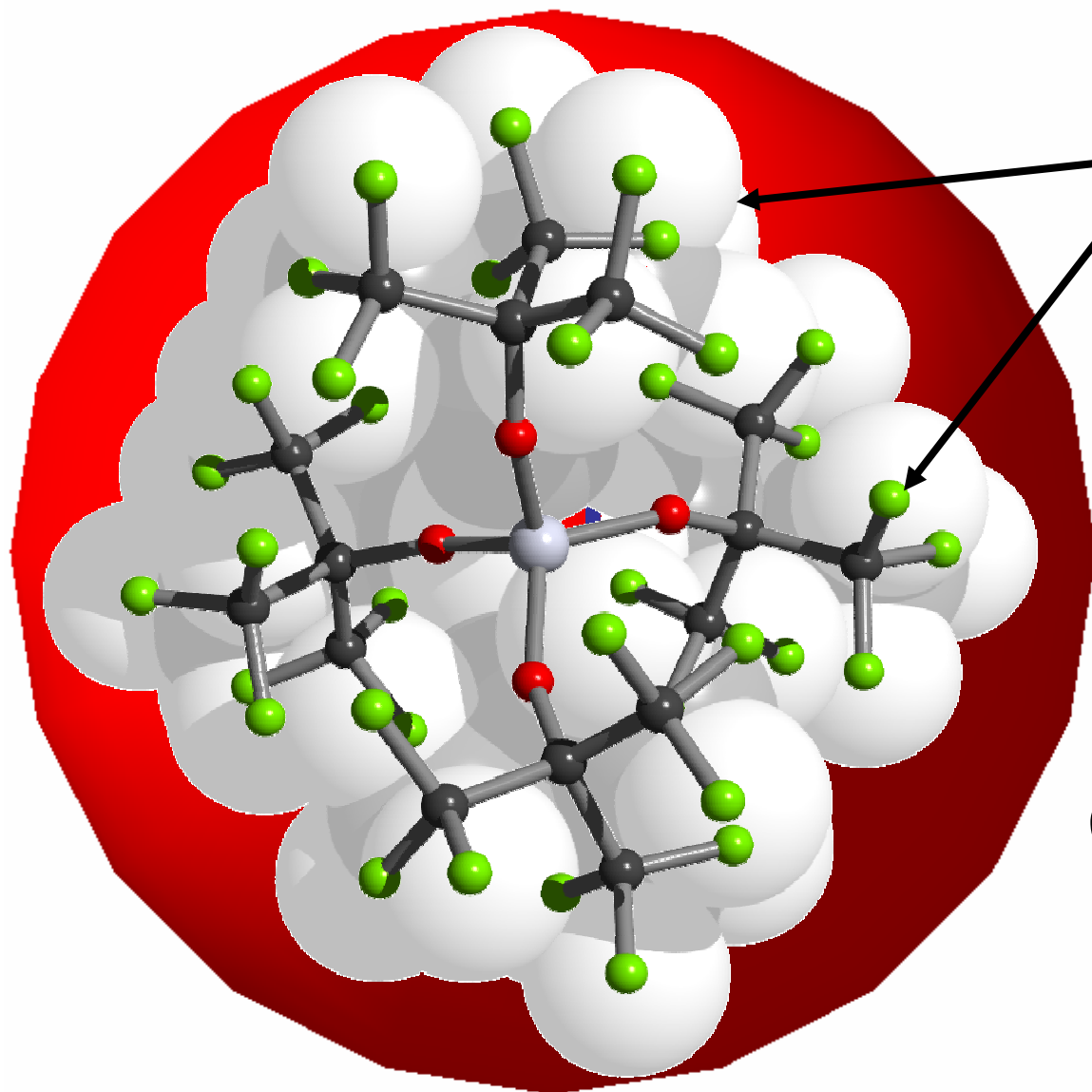
Chemistry with Weakly
Coordinating Anions...

What are weakly coordinating anions...?

- Large anions of low basicity...
- ...that minimize cation-anion interactions.

I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116-2142.

[Teflon]⁻...?



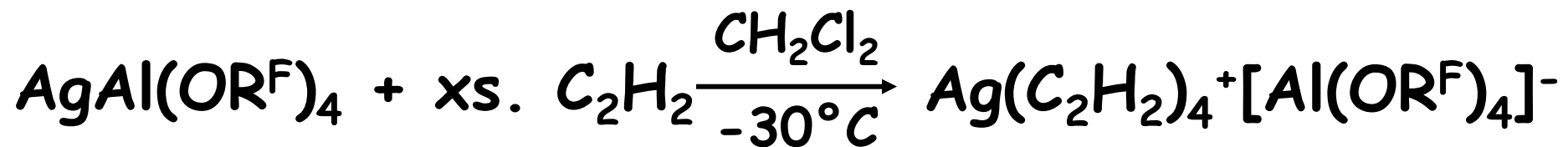
Surface C-F Bonds:

=> Teflon!

Large Volume:

=> $\text{Cl}^- < [\text{PF}_6]^- < \text{„[Teflon]}^- \text{“}$
or
 $0.035 < 0.100 < 0.750 \text{ nm}^3$



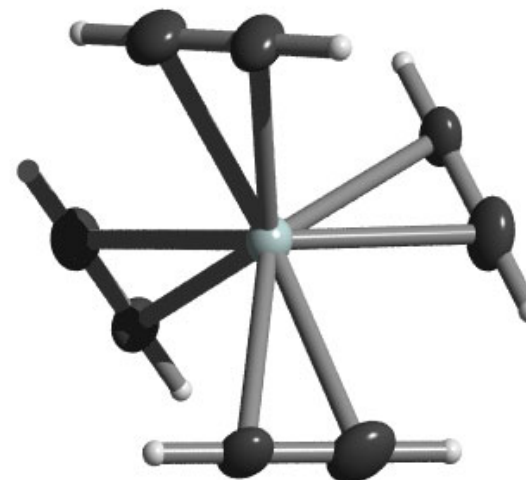
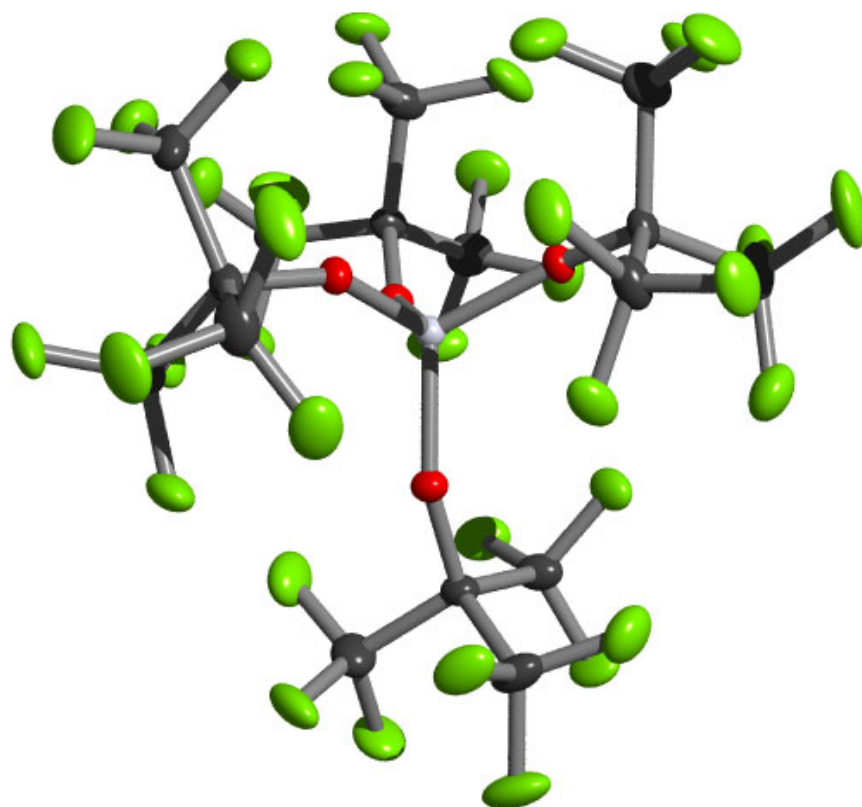


R = C(CF₃)₃

A. Reisinger 2003-6.

Tetragonal

$\bar{I}4$



T = 150 K

T = 100 K

R1 = 0.0252,

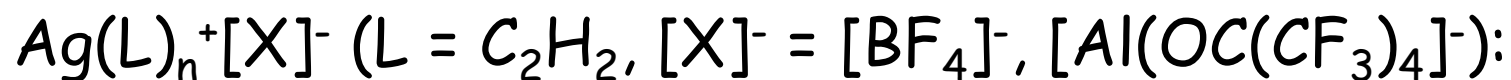
R1 = 0.0286

wR2 = 0.0660

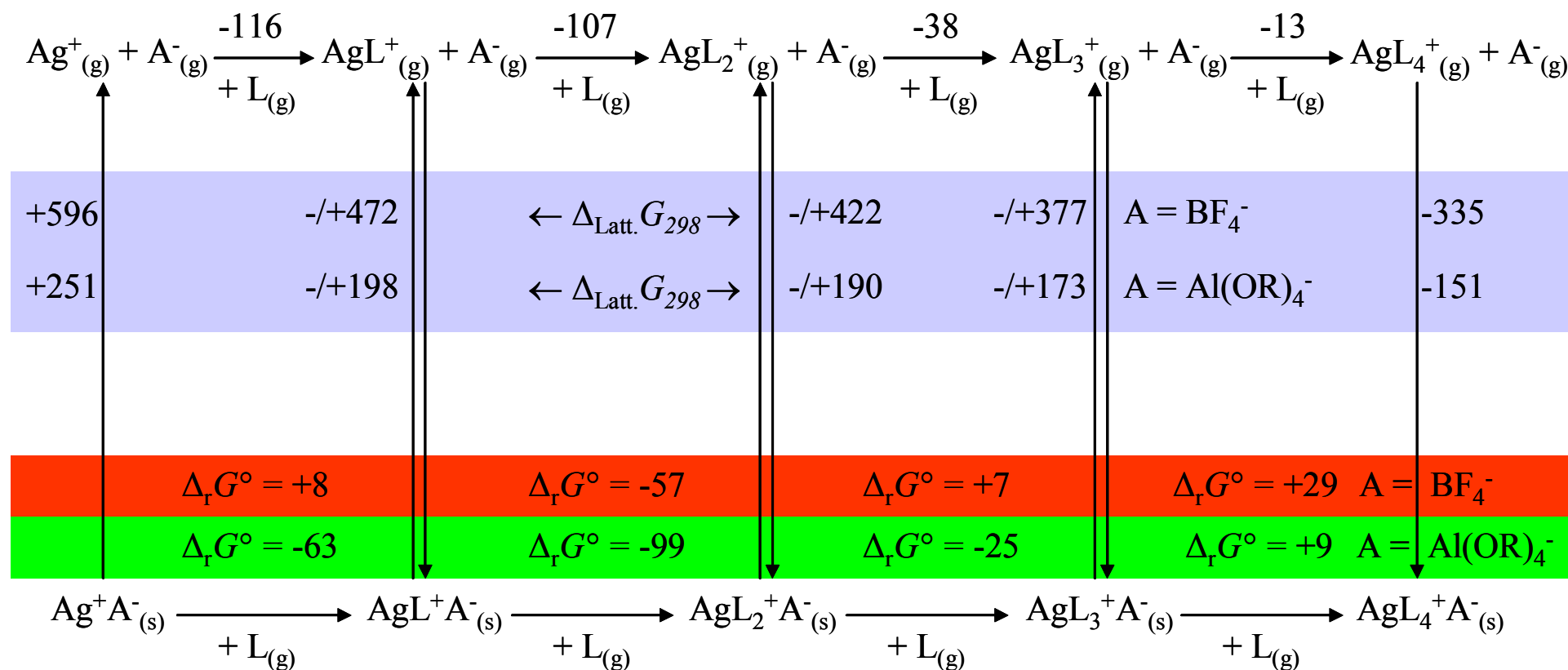
wR2 = 0.0687

2 $\theta_{\text{max.}}$ = 54°

2 $\theta_{\text{max.}}$ = 54°

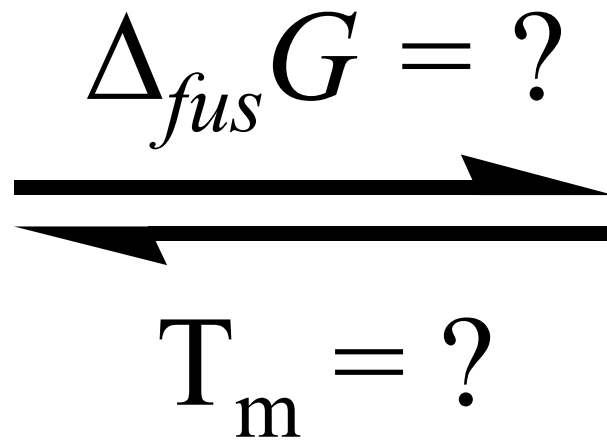


Relating Solid State and Gas Phase Stability



A Born-Haber-Cycle Approach ($\Delta_r G^\circ$ in kJ mol⁻¹)

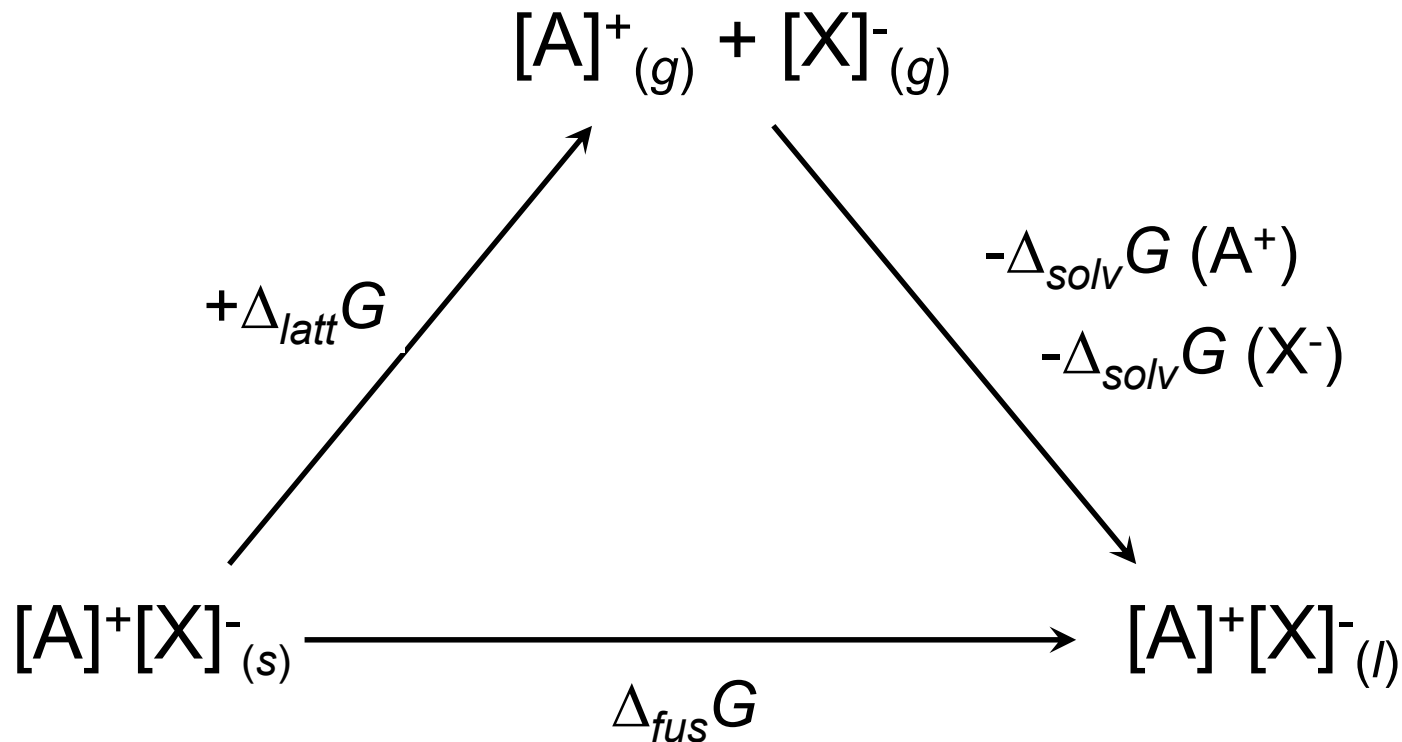
The basic Question...



And more...



Why are ILs Liquid?



- The sign of $\Delta_{fus}G$ tells us if the solid or liquid state is thermodynamically favored at a given temperature.

Calculation of $\Delta_{latt}G$

$$\Delta_{latt}G = \Delta_{latt}H - T\Delta_{latt}S$$

- $\Delta_{latt}H$ estimated using volume based thermodynamics (VBT)*
 - U_{POT} (and thus $\Delta_{latt}H$) for a 1:1 [A][X] salt is proportional to the cube root of its molecular volume (V_m):

$$U_{POT} = 2 \left(\frac{\alpha}{\sqrt[3]{V_m}} + \beta \right)$$

- Where α and β are empirical constants of best fit.
- Essentially a volume based Kapustinskii equation.

* Glasser and Jenkins, *Chem. Soc. Rev.*, 2005, **34**, 866.

Calculation of $\Delta_{latt}G$

$$\Delta_{latt}G = \Delta_{latt}H - T\Delta_{latt}S$$

- $\Delta_{latt}S = \{S_{(g)}[A]^+ + S_{(g)}[X]^- \} - S_{(s)}[A][X]$
 - $S_{(g)}(A^+)$ and $S_{(g)}(X^-)$ from DFT calculations (BP86/SV(P)) using TURBOMOLE.
 - $S_{(s)}[A][X]$ estimated using VBT.

$$S_{298}^{\circ} = kV_m + c$$

- Where k and c are empirical constants of best fit.

Assessment of V_m

- Molecular volumes (V_m) are the basis of VBT.
- V_m for a salt is the sum of the ion volumes (V_{ion}) of each ion as determined from assessment of X-ray structures.*

$$V_{ion}(A^+) = \frac{V_{cell}(A^+X^-)}{Z} - V_{ion}(X^-)$$

- If no X-ray structure containing the desired ion is known then V_{th} can often be estimated from related ions.
- Errors in V_m do not lead to large errors in VBT calculations for ILs – typically less than 5 – 10 kJ mol⁻¹ for U_{POT} .

* Jenkins *et al.*, *Inorg. Chem.*, 1999, **38**, 3609.

V_{ion} from X-ray Data

Cations	V_{ion} (nm ³)	Anions	V_{ion} (nm ³)
[EMIM] ⁺	0.156 ±0.018	[BF ₄] ⁻	0.073 ±0.009
[C ₃ MIM] ⁺	0.178 ±0.028	[PF ₆] ⁻	0.109 ±0.008
[BMIM] ⁺	0.196 ±0.021	[TfO] ⁻	0.131 ±0.015
[C ₅ MIM] ⁺	0.219 ±0.015	[Tf ₂ N] ⁻	0.232 ±0.015
[BMMIM] ⁺	0.229 ±0.012		
[BPy] ⁺	0.198 ±0.013		
[BMPyr] ⁺	0.221 ±0.015		
[C ₅ MPyr] ⁺	0.238 ±0.018		
[C ₅ NEt ₃] ⁺	0.268 ±0.016		

Calculation of $\Delta_{sol/v}G$

- $\Delta_{sol/v}G$ for each ion was calculated using the COSMO¹⁾ module of TURBOMOLE - requires the dielectric constant of the IL.

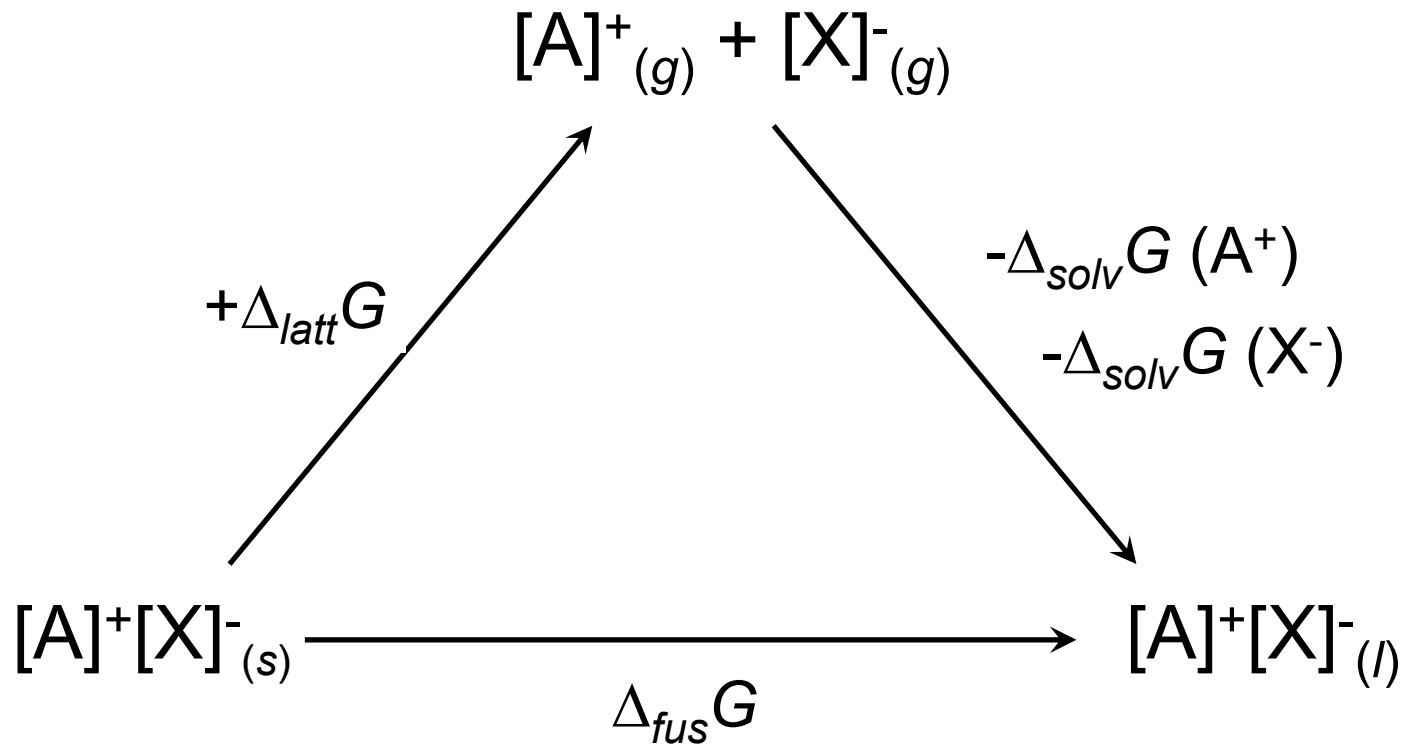
Salt	From E_T^N values	From keto-enol tautomerisation	From dielectric spectroscopy
[BMIM][BF ₄]	~ 25	46	11.7
[BMIM][PF ₆]	~ 25	52	11.4

- 14 highly pure room-temperature ILs were synthesised in collaboration with Paul Dyson (EPFL).
- Their dielectric constants (*dcs*) were determined in collaboration with Hermann Weingärtner (Bochum).²⁾

1) A. Klamt, G. J. Schüürmann, *Chem. Soc. Perkin Trans. 2*, **1993**, 799-805.

2) H. Weingärtner et al., *J. Phys. Chem. B*, **2006**, 110, 12682.

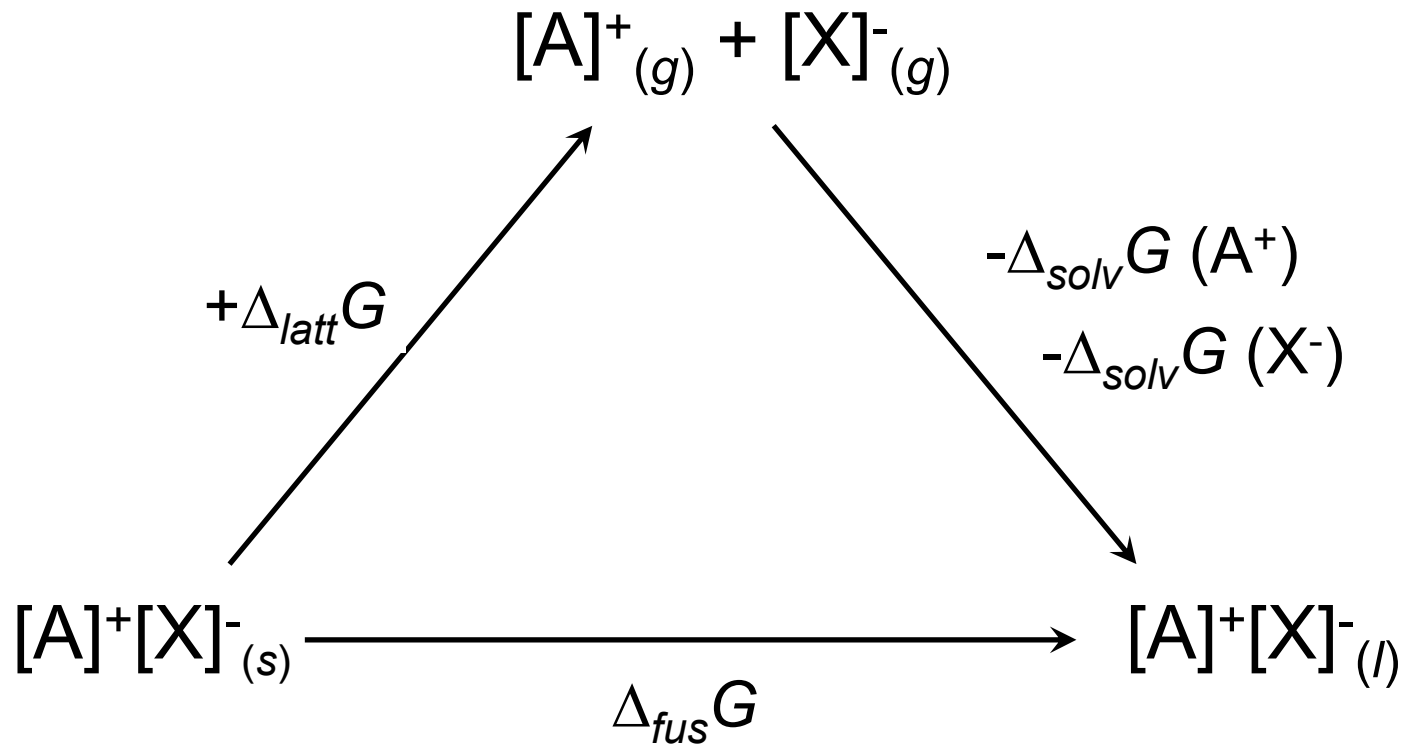
Closing the cycle...!



1.) Standard conditions (298 K, 1 bar).

Salt Name	m.p. (°C)	$\Delta_{fus}G^\circ$ (kJ mol ⁻¹)
[EMIM][BF ₄]	15 to -1‡	-23
[EMIM][TfO]	-9 to -15‡	-41
[EMIM][Tf ₂ N]	-19	-44
[C ₃ MIM][Tf ₂ N]	Not observed.	-45
[BMIM][BF ₄]	Not observed.	-37
[BMIM][PF ₆]	9	-25
[BMIM][TfO]	13	-49
[BMIM][Tf ₂ N]	-5	-50
[BMMIM][Tf ₂ N]	Not observed.	-52
[C ₅ MIM][Tf ₂ N]	-10	-55
[BPy][Tf ₂ N]	23	-43
[BMPyr][Tf ₂ N]	-9	-45
[C ₅ MPyr][Tf ₂ N]	8	-45
[C ₅ NEt ₃][Tf ₂ N]	0	-43

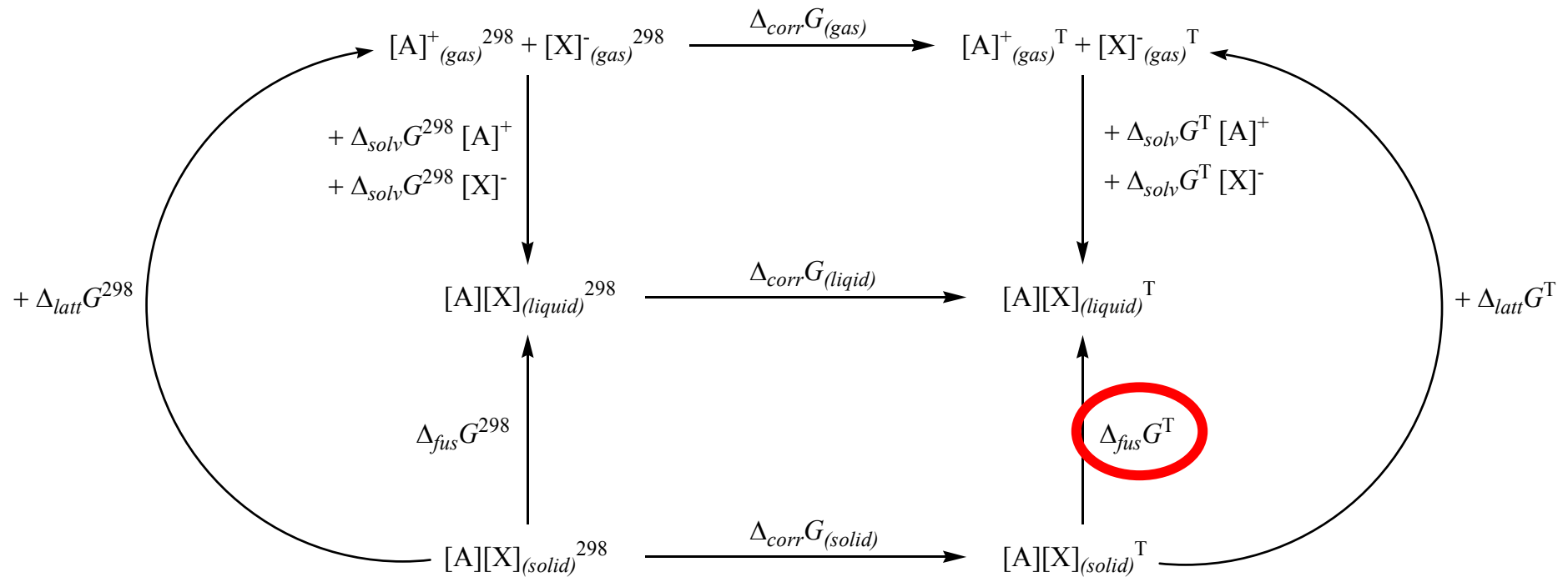
Closing the cycle...!



2.) Melting point prediction:

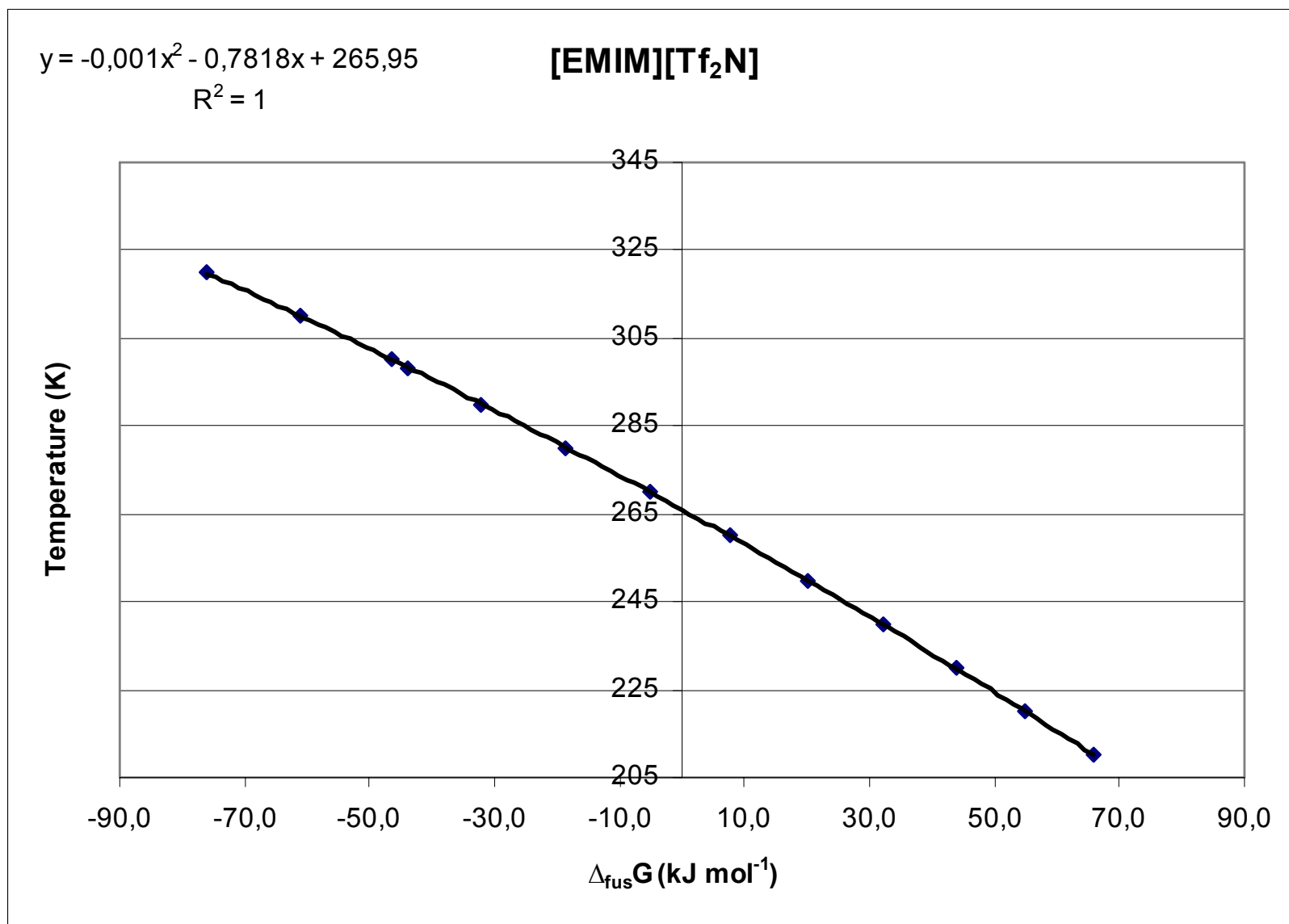
Plotting ΔG vs. Temperature.

Calculating $\Delta_{fus} G^T$

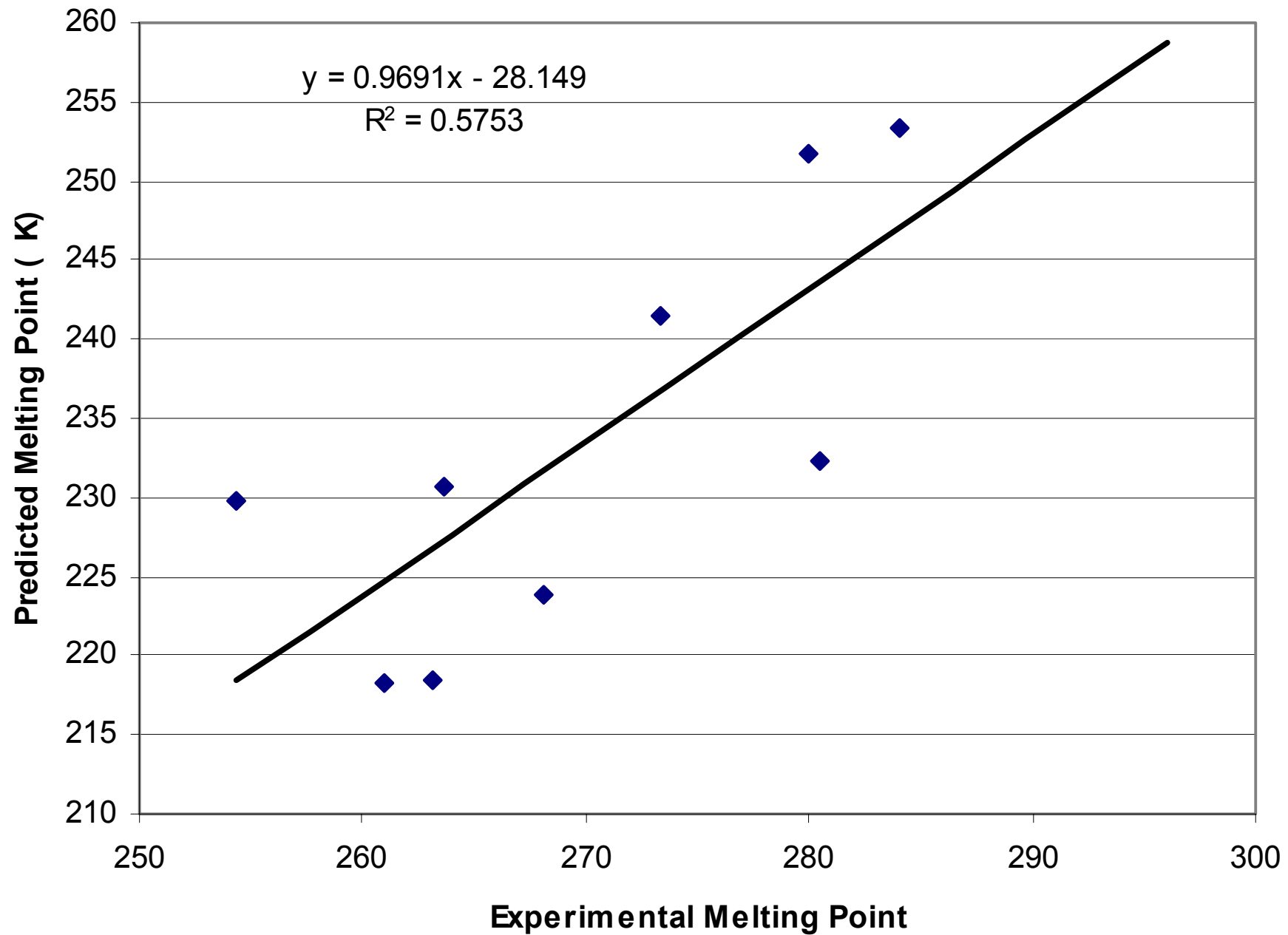


Must make the approximation that $\Delta_{solv} G^{298} = \Delta_{solv} G^T$

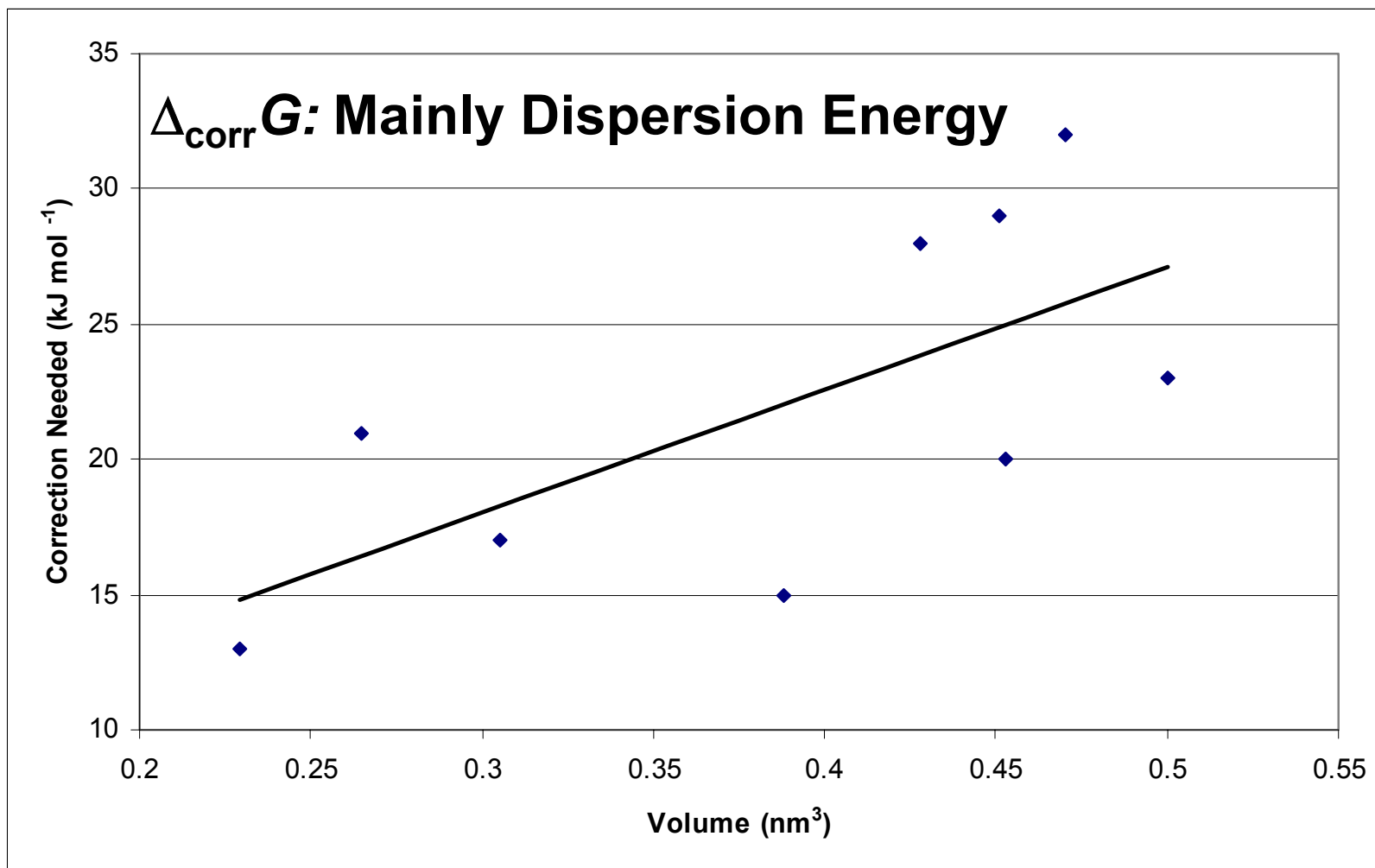
Melting point prediction: Plotting ΔG vs. Temperature



Salt Name	m.p. (°C)	$\Delta_{fus} G^\circ$ (kJ mol ⁻¹)	Predicted m.p. (°C)
[EMIM][BF ₄]	15 to -1 [‡]	-23	-21
[EMIM][TfO]	-9 to -15 [‡]	-41	-55
[EMIM][Tf ₂ N]	-19	-44	-43
[C ₃ MIM][Tf ₂ N]	Not observed.	-45	-43
[BMIM][BF ₄]	Not observed.	-37	-47
[BMIM][PF ₆]	9	-25	-20
[BMIM][TfO]	13	-49	-65
[BMIM][Tf ₂ N]	-5	-50	-49
[BMMIM][Tf ₂ N]	Not observed.	-52	-49
[C ₅ MIM][Tf ₂ N]	-10	-55	-55
[BPy][Tf ₂ N]	23	-43	-41
[BMPyr][Tf ₂ N]	-9	-45	-42
[C ₅ MPyr][Tf ₂ N]	8	-45	-41
[C ₅ NEt ₃][Tf ₂ N]	0	-43	-32



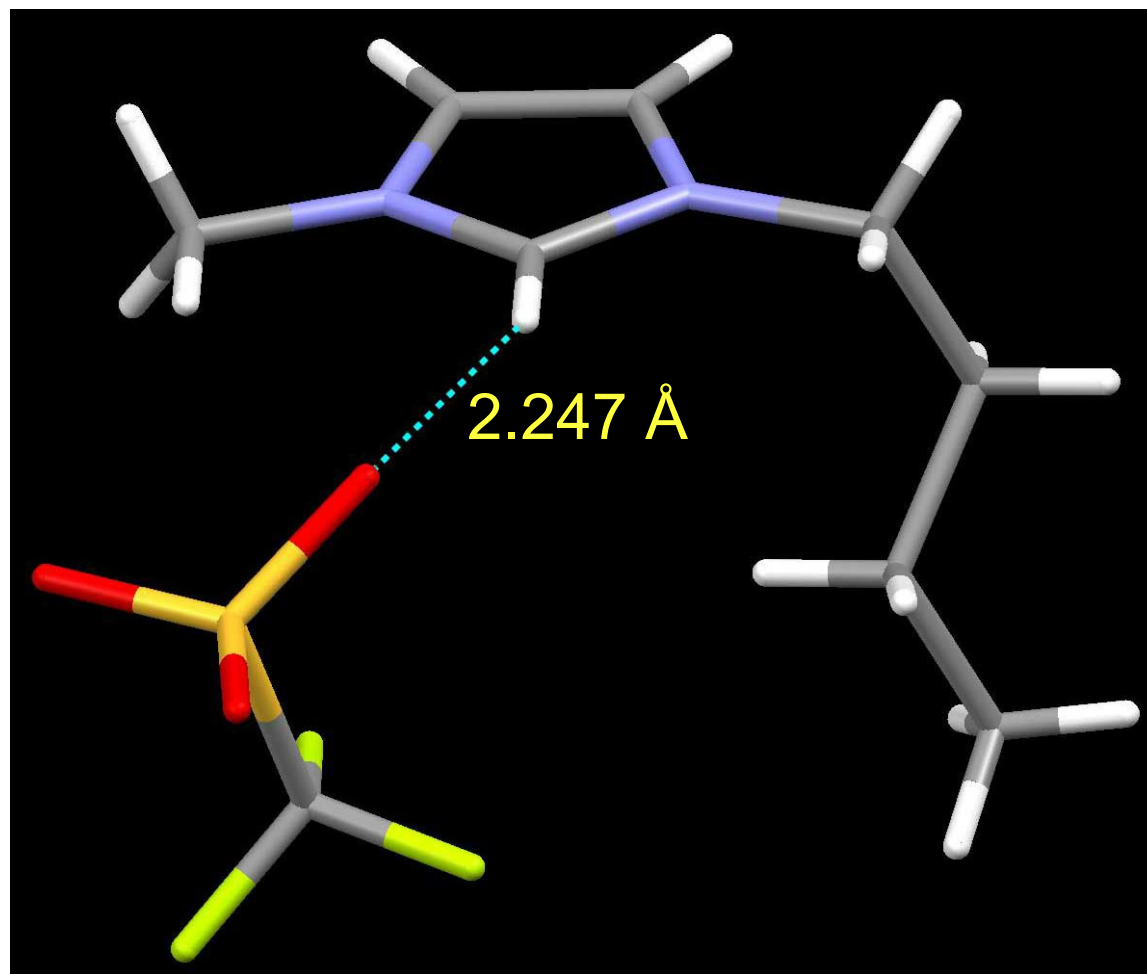
An Empirical Correction Factor



$$\Delta_{\text{corr}} G = 45 \frac{\text{kJmol}^{-1}}{\text{nm}^3} \cdot V_m + 5 \text{kJmol}^{-1}$$

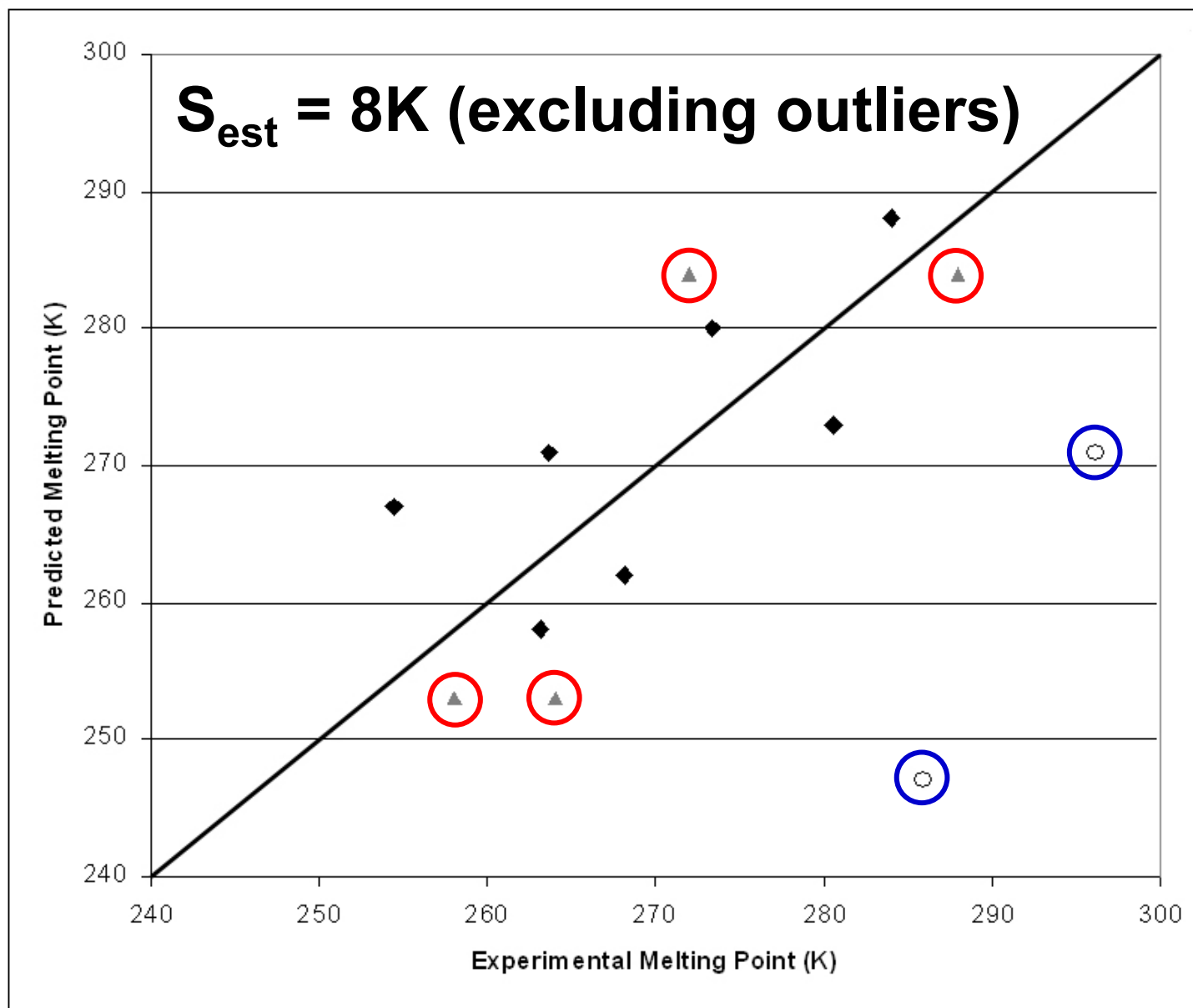
Salt Name	m.p. (°C)	$\Delta_{fus} G^\circ$ (kJ mol ⁻¹)	Predicted m.p. Corrected (°C)
[EMIM][BF ₄]	15 to -1 [‡]	-23	11
[EMIM][TfO]	-9 to -15 [‡]	-41	-20
[EMIM][Tf ₂ N]	-19	-44	-6
[C ₃ MIM][Tf ₂ N]	Not observed.	-45	-6
[BMIM][BF ₄]	Not observed.	-37	-11
[BMIM][PF ₆]	9	-25	15
[BMIM][TfO]	13	-49	-26
[BMIM][Tf ₂ N]	-5	-50	-11
[BMMIM][Tf ₂ N]	Not observed.	-52	-10
[C ₅ MIM][Tf ₂ N]	-10	-55	-15
[BPy][Tf ₂ N]	23	-43	-2
[BMPyr][Tf ₂ N]	-9	-45	-2
[C ₅ MPyr][Tf ₂ N]	8	-45	0
[C ₅ NEt ₃][Tf ₂ N]	0	-43	7

Structure of [BMIM][TfO]



A. R. Choudhury *et al.*, *J. Am. Chem. Soc.*, 2005, **127**, 16792.

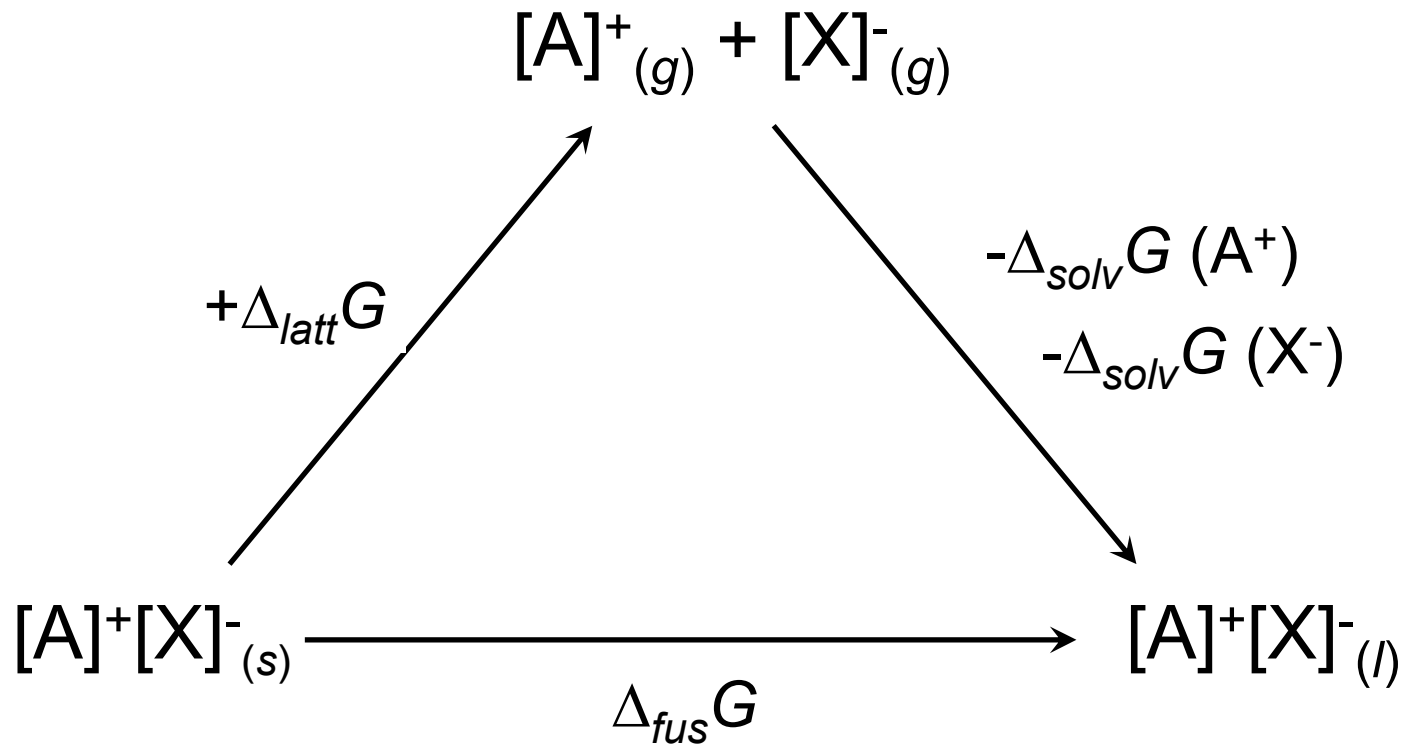
Experimental vs. predicted melting points



Grey data points include literature data for [EMIM][BF₄] and [EMIM][TfO] (Max. and Min. values).

Open circles are the outliers (H-bonding, π -stacking...!).

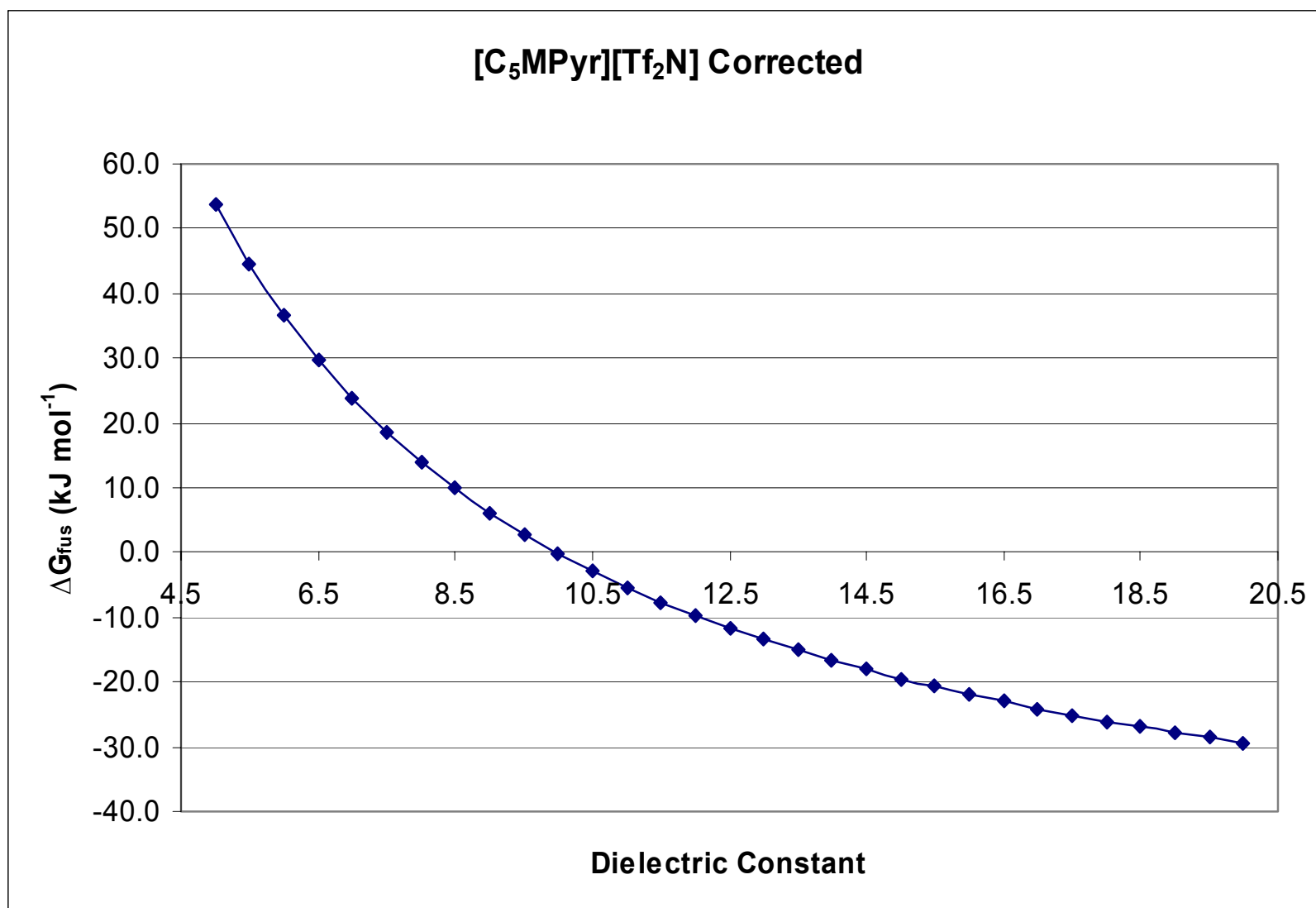
Closing the cycle...!



3.) Dielectric constant prediction:

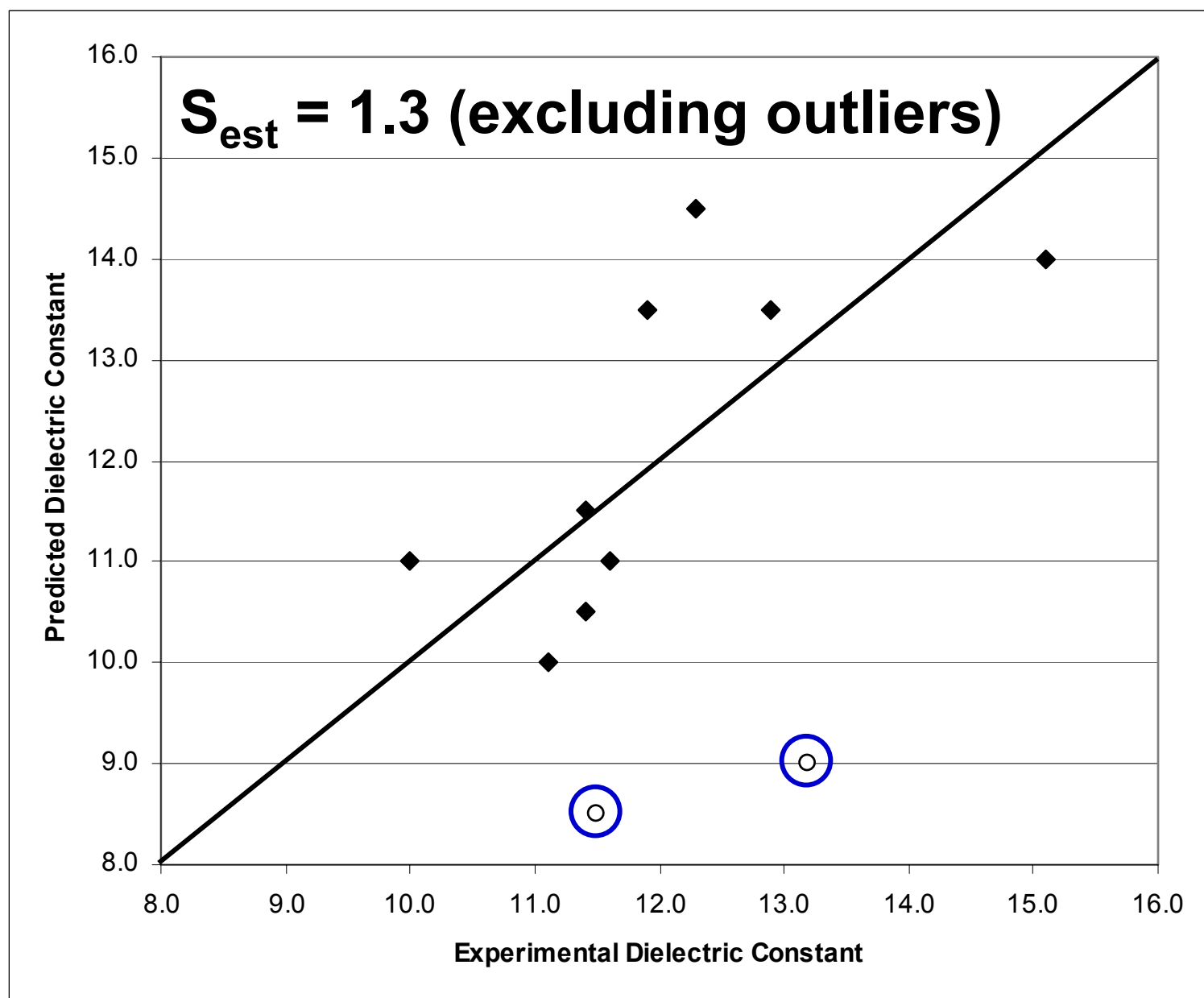
Plotting ΔG with various ϵ_r vs. m.p..

Dielectric constant prediction: Plotting ΔG with various ϵ_r vs. m.p.



Salt Name	Dielectric Constant (± 0.3)	Predicted Dielectric Constant Corrected
[EMIM][BF ₄]	12.9	13.5
[EMIM][TfO]	15.1	14.0
[EMIM][Tf ₂ N]	12.3	14.5
[C ₃ MIM][Tf ₂ N]	11.8	*
[BMIM][BF ₄]	11.7 [‡]	*
[BMIM][PF ₆]	11.4 [‡]	11.5
[BMIM][TfO]	13.2	9.0
[BMIM][Tf ₂ N]	11.6	11.0
[BMMIM][Tf ₂ N]	11.5	*
[C ₅ MIM][Tf ₂ N]	11.4	10.5
[BPy][Tf ₂ N]	11.5	8.5
[BMPyr][Tf ₂ N]	11.9	13.5
[C ₅ MPyr][Tf ₂ N]	11.1	10.0
[C ₅ NEt ₃][Tf ₂ N]	10.0	11.0

Experimental vs. predicted dielectric constants



Open circles are the outliers (H-bonding, π -stacking...!).

Summary I

- The melting of salts to give a ILs can be understood by a simple Born-Haber cycle.
- The contributing thermodynamic functions may be ***approximated*** by a combination of volume based thermodynamics and quantum chemical calculations.
- An understanding of the contributions to the Born-Haber cycle allows one to systematically improve ILs on the basis of easily accessible calculated data.

Outlook

- Application of solvation methods that do not need dielectric constant (COSMO-RS).
- Assessment of $\Delta_{\text{solv.}}G$ temperature dependent.
- Inclusion of Dispersion to lattice energies.

=> Predictions from scratch, no experimental known required.....!

Prediction of Viscosities, Conductivities, Densities...

- Is it possible to also predict other physical properties ...?

Hole Theory

- Volume of molten salts increases upon melting.
=> Creating free space between the ions.
- In order for ions in an IL to move they must find themselves next to a hole that is suitably large to permit movement.
- probability, P , of finding a hole of radius, r , in a liquid:

$$Pdr = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2} dr$$

$a = 4\pi\gamma/kT$,
 Γ : surface tension of the liquid,
 K : Boltzmann constant
 T : absolute temperature.

(1) Abbott, A. P. ChemPhysChem **2004**, 5, 1242-1246.

(2) Abbott, A. P. ChemPhysChem **2005**, 6, 2502-2505.

Hole Theory: Viscosity Prediction

$$\eta = \frac{m\bar{c} / 2.12\sigma}{P(r > R_{+/-})}$$

\bar{c} is the average speed of the particle $[(8R_{+/-}T/\pi m)^{1/2}]$.
 σ is the collision diameter of the particle $[4\pi(R_{+/-})^2]$.

=>Predictions made for ILs are more scattered than those for molecular liquids.

=>Standard error of the estimate ($s_{est} = 419$ cP) is rather large.

(1) Abbott, A. P. ChemPhysChem **2004**, 5, 1242-1246.

(2) Abbott, A. P. ChemPhysChem **2005**, 6, 2502-2505.

Hole Theory: Conductivity Prediction

$$\kappa = \frac{z^2 F e \rho}{6 \pi \eta M_w} (R_+^{-1} + R_-^{-1})$$

z is the ion charge, F is the Faraday constant, e is the electronic charge, ρ is the density of the IL, M_w is the molecular weight of the IL, R_+ and R_- are the ionic radii.

=>Conductivities of 30 ILs predicted ($r^2 = 0.92$): $s_{est} = 0.2 \text{ mScm}^{-1}$

=>Not suitable for predicting the conductivities of unknown salts:
Density and viscosity of the IL must be known...!

(1) Abbott, A. P. ChemPhysChem **2004**, 5, 1242-1246.

(2) Abbott, A. P. ChemPhysChem **2005**, 6, 2502-2505.

V_m as an Ordering Principle

$$U_{POT} = 2 \left(\frac{\alpha}{\sqrt[3]{V_m}} + \beta \right) \quad S_{298}^{\circ} = kV_m + c$$

- => V_m is a physical observable (x-ray).**
- => V_m may be viewed as measure for the size of the ions.**
- => Size often governs physical properties...!**
- => Is V_m an ordering principle for physical properties of ILs...?**

ILs used for the V_m Correlations...

Tf ₂ N ILs	BF ₄ ILs	PF ₆ ILs	N(CN) ₂ ILs	Nitrile functionalised fluorometallate ILs
EMIM	BMIM	BMIM	EMIM	C2(CN)MIM[BF ₄]
C3MIM	C6MIM	C6MIM	BMIM	C3(CN)MIM[BF ₄]
BMIM	C8MIM	C8MIM	BMPyr	C4(CN)MIM[BF ₄]
BPy				C4(CN)MIM[PF ₆]
C5MIM				
BMPyr				
BMMIM				
C5MPyr				
C5NEt ₃				
SEt ₃				
SMePh ₂				
BMPyr				
C4NMe ₃				

All physical data from **highly purified ILs** of the labs of either Paul Dyson at EPFL or IOLITEC in Freiburg.

Der Teil über die Korrelation der physikalischen Eigenschaften mit V_m ist noch nicht publiziert und daher aus dem Vortrag entfernt.

Bei Fragen Rückmeldung an mich...

krossing@uni-freiburg.de

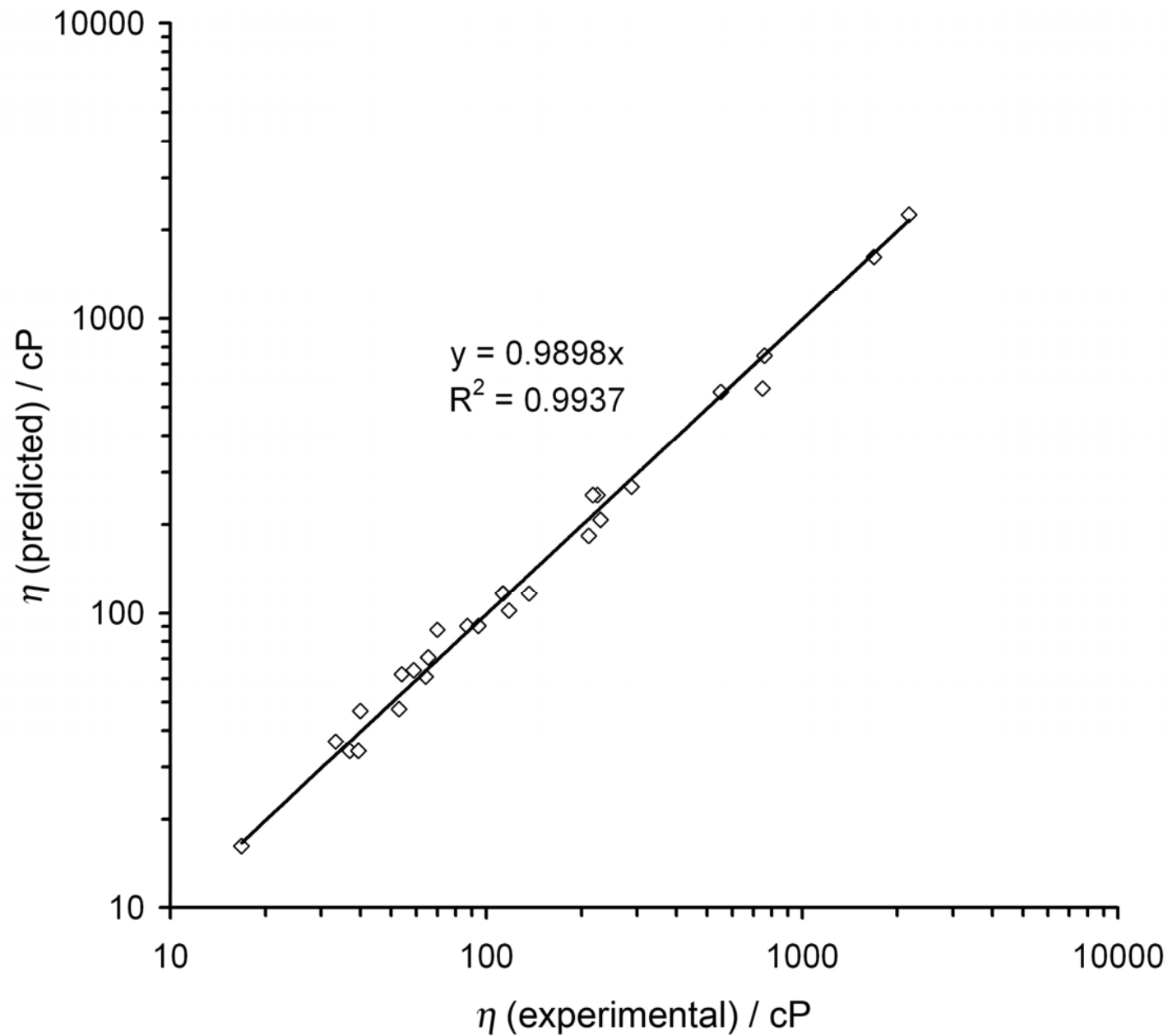
V_m as an Ordering Principle

1.) Viscosities...

(26 ILs, η = 16.8 to 2180 cP)

**All physical data from highly purified ILs of the labs
of either Paul Dyson at EPFL or IOLITEC in Freiburg.**

Experimental vs. Predicted Viscosities



V_m as an Ordering Principle

2.) Conductivities...

(22 ILs, $\sigma = 0.29$ to 6.63 mS cm^{-1})

**All physical data from highly purified ILs of the labs
of either Paul Dyson at EPFL or IOLITEC in Freiburg.**

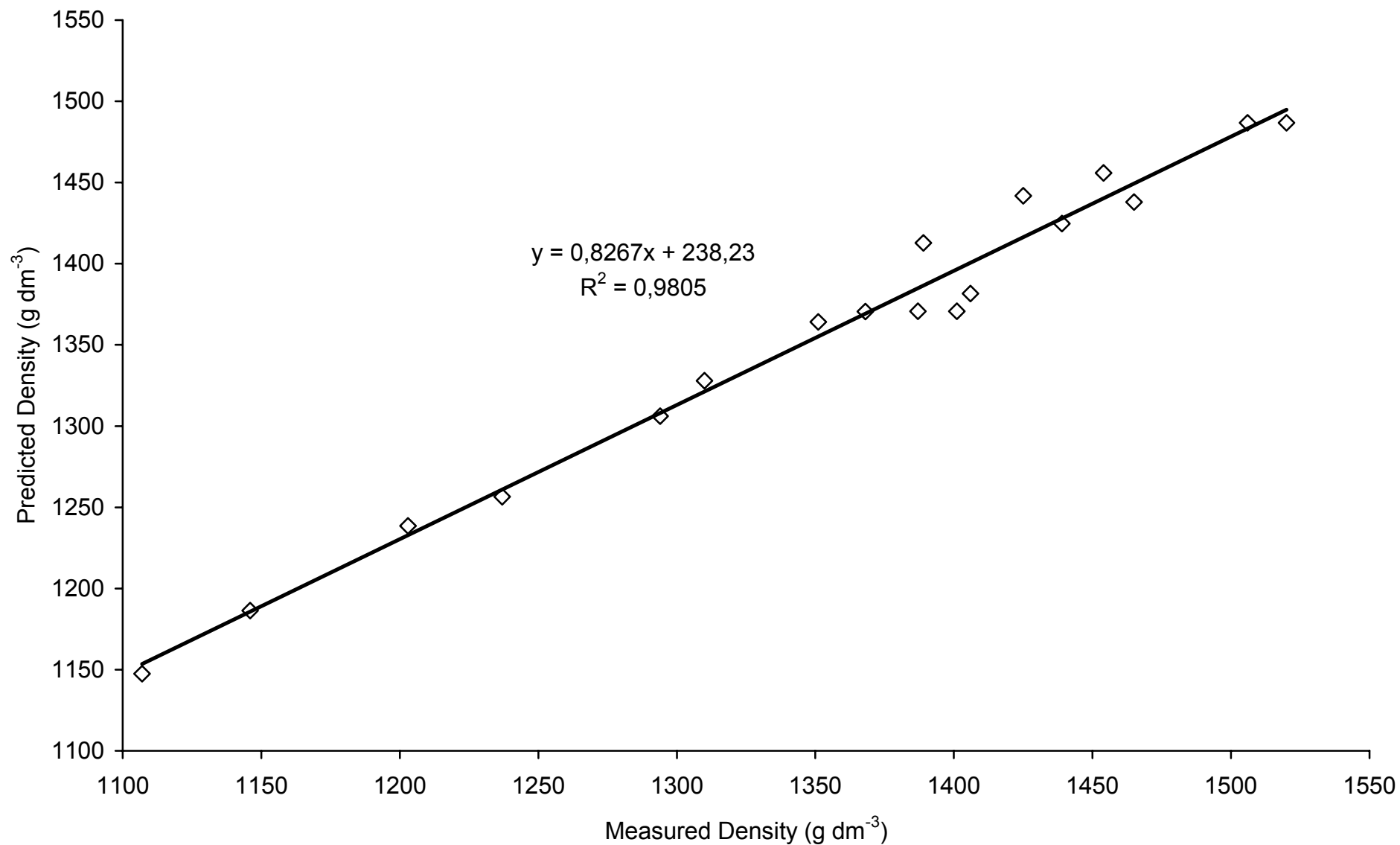
V_m as an Ordering Principle

3.) Densities...

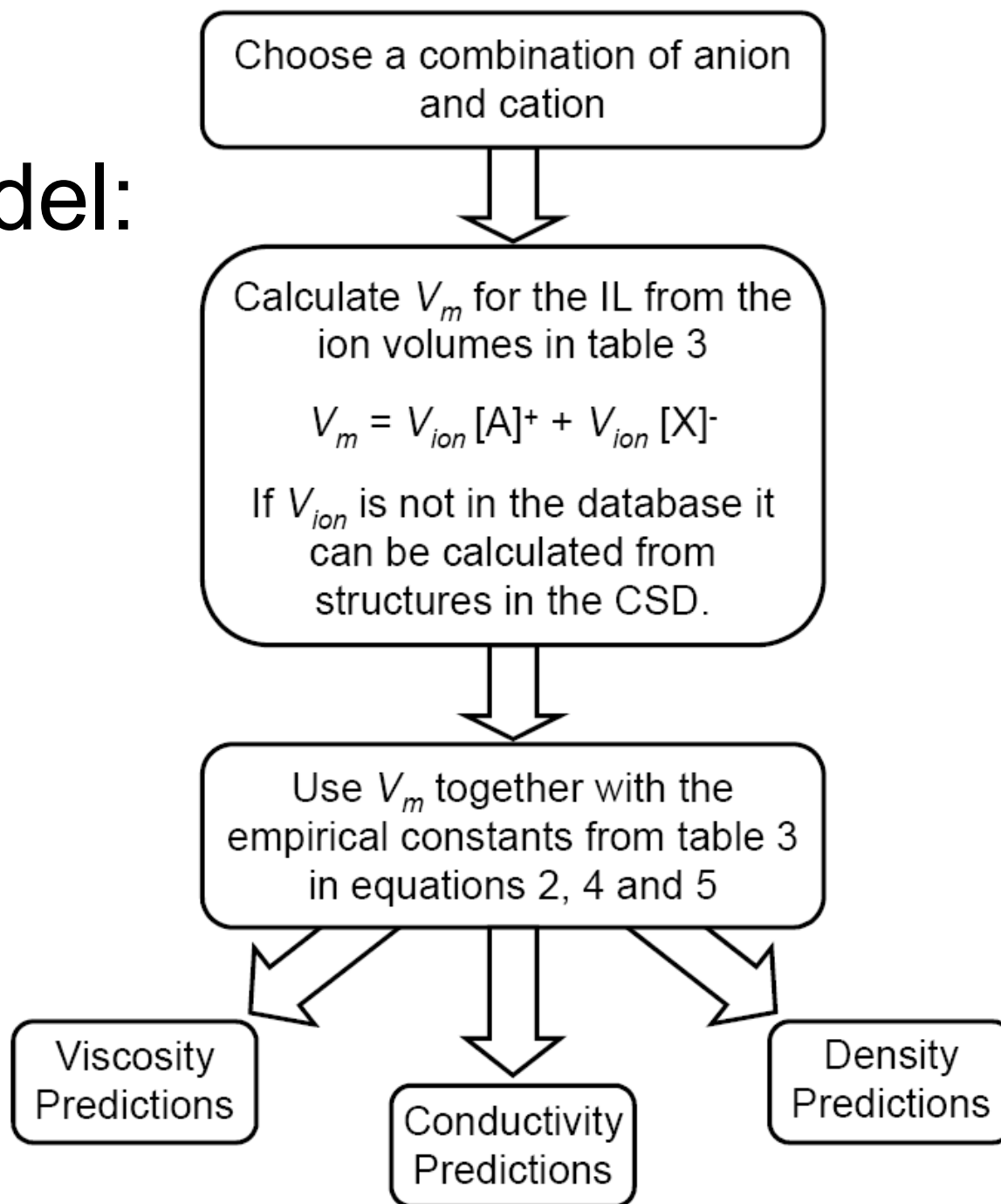
(22 ILs, $\rho = 1.023$ to 1.520 kg dm^{-3})

**All physical data from highly purified ILs of the labs
of either Paul Dyson at EPFL or IOLITEC in Freiburg.**

Predicted vs. experimental Densities



Using the model:



Summary II

- The physical properties of ILs are highly-correlated with their molecular volumes (V_m).
- The empirical relationships that arise from this can be used to predict the viscosities, conductivities and densities of ILs.
- These predictions are fast and simple to apply and do not require any special knowledge or equipment.

Ziel

- Vorhersage der physikalischen Eigenschaften von ILs mit einer Genauigkeit von 10 % ohne jegliches Vorwissen...!

Thank you...

Lausanne:

Paul Dyson

Corinne Daguenet

Freiburg:

John Slattery, Safak Bulut

Thomas Schubert

IOLITEC

Bochum:

Hermann Weingärtner

Alla Oleinikova

[illegible]

EPFL, Albert-Ludwigs-Universität Freiburg,

SNF, Roche-Foundation, DFG (SPP 1191), IOLITEC

[illegible]