JÜLICH
FORSCHUNGSZENTRUM

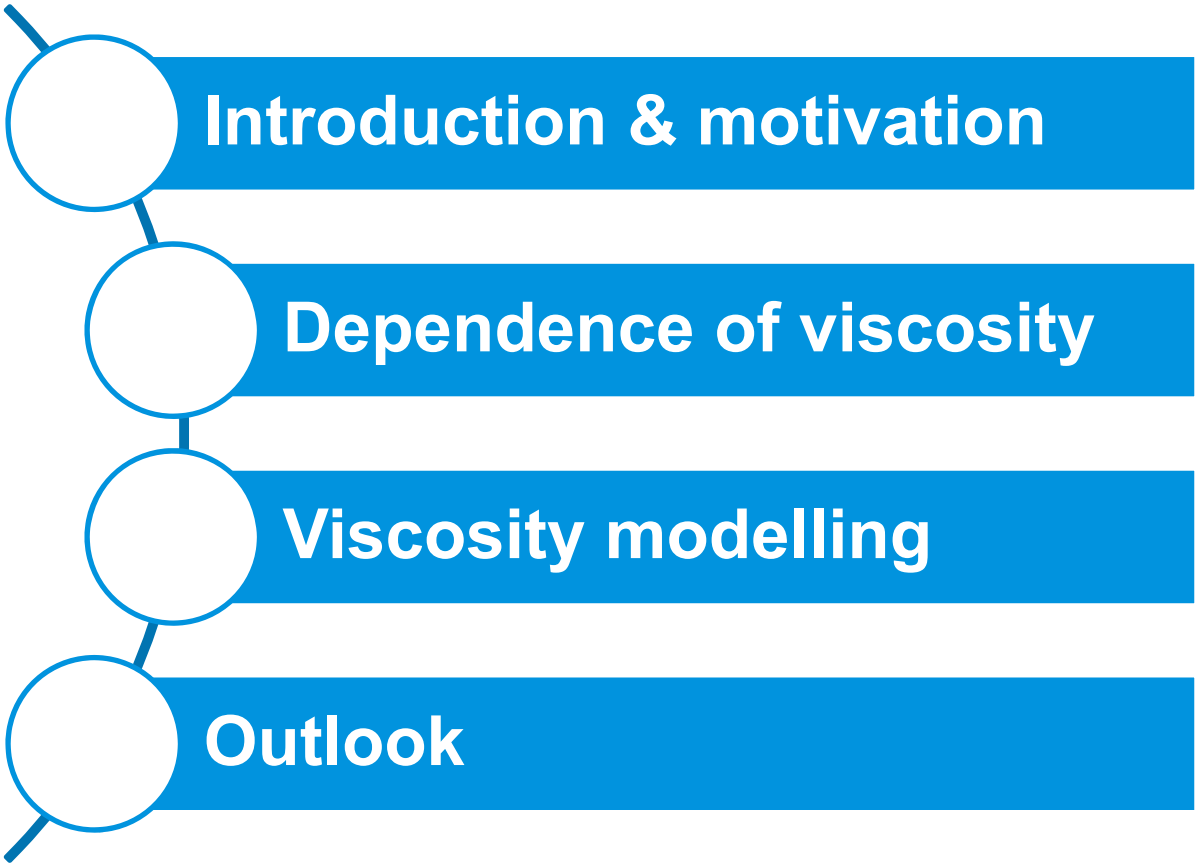
Modelling viscosity of molten oxides (HotVeGas Part II)

30.06.2016 Guixuan Wu[1], Elena Yazhenskikh[1], Klaus Hack[2], and Michael Müller[1]

[1] IEK-2, Forschungszentrum Jülich GmbH, Germany
[2] GTT Technologies, Herzogenrath, Germany

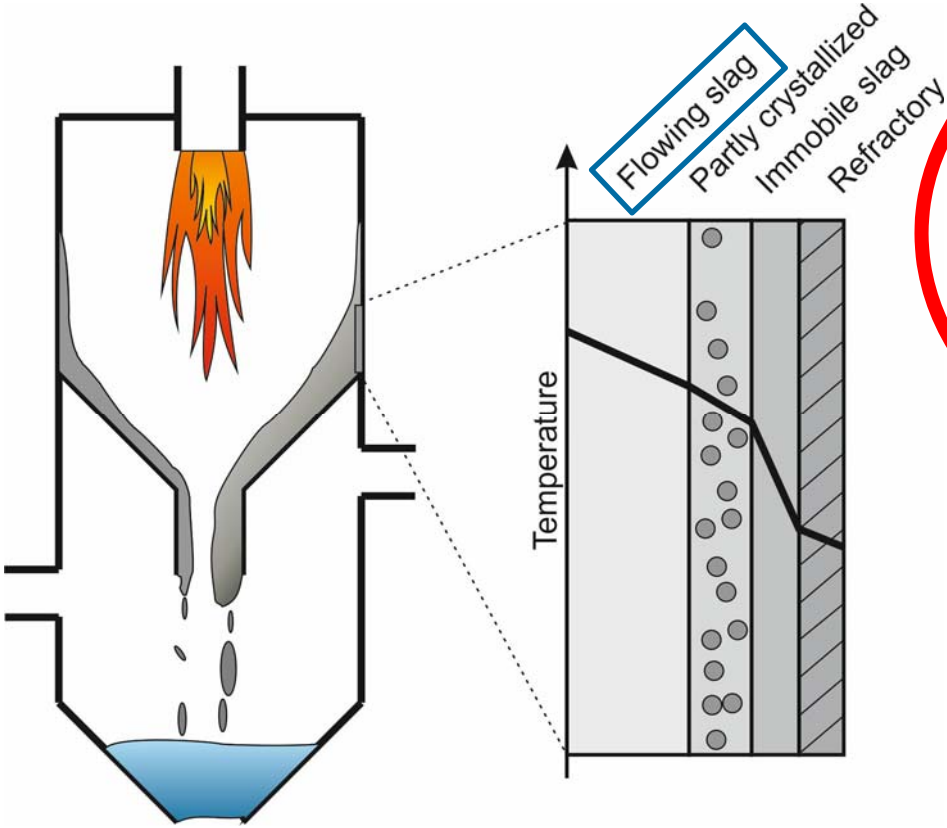
GTT Annual Users' Meeting 2016

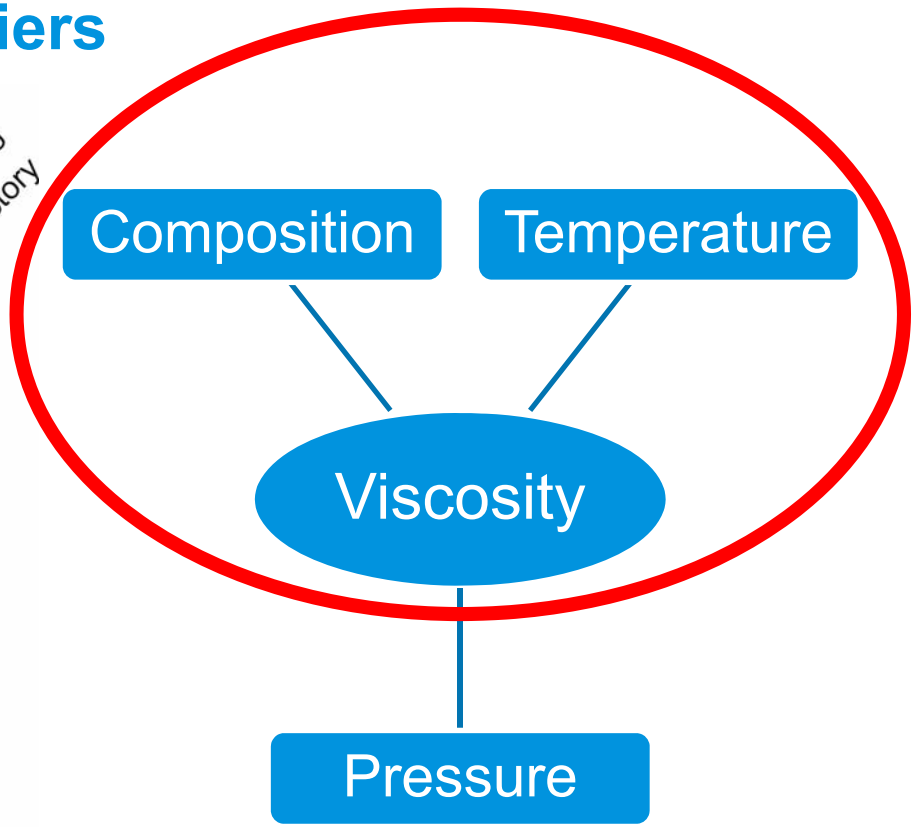
Outline


Introduction & motivation
Dependence of viscosity
Viscosity modelling
Outlook

Introduction & motivation

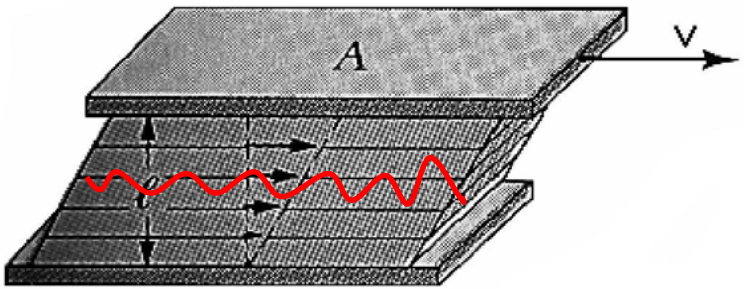
Entrained-flow slagging gasifiers



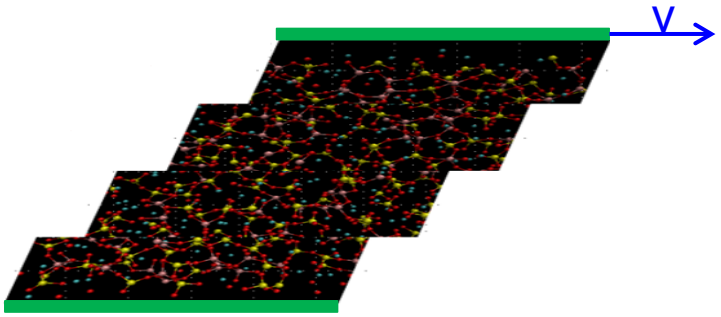


Classical model: Comp. Temp. → Viscosity

Idea of modelling

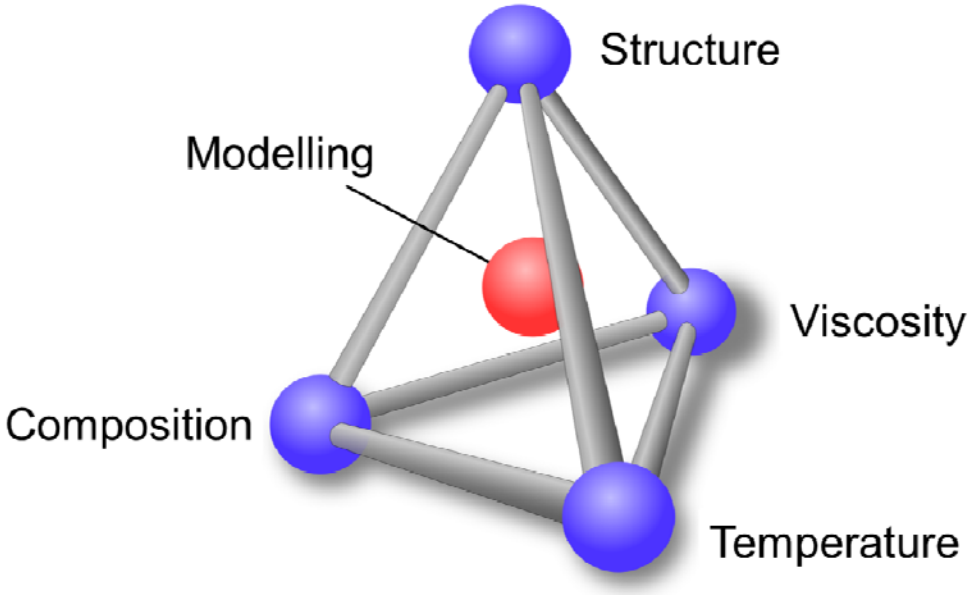


Viscosity: **Internal fluid friction**



Multicomponent oxide melts

Modelling ⟷ Fitting



Idea of modelling

JÜLICH FORSCHUNGSZENTRUM

Thermodynamic database

↓

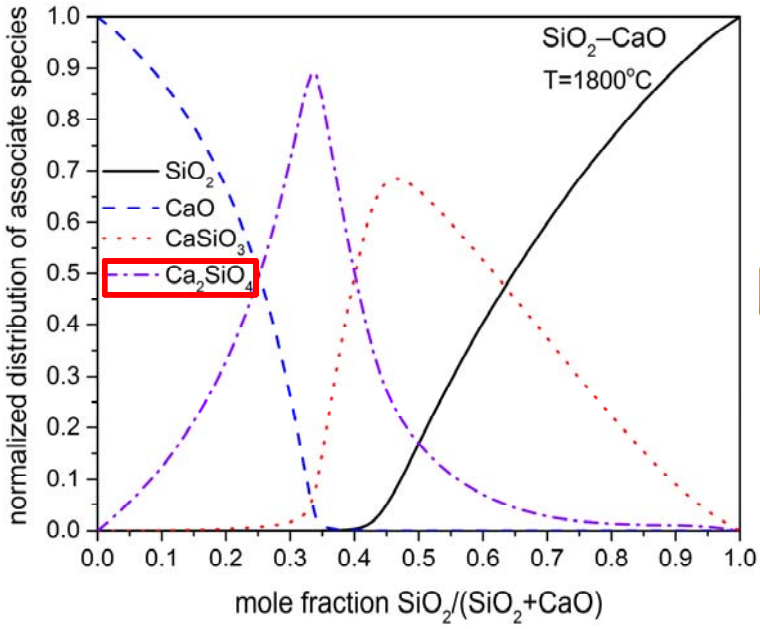
Associate species

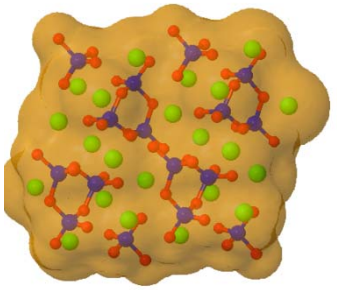
↓

Structural units

↓

Determination of Viscosity contribution





$CaSiO_3$

Viscosity ↔ **Bond strength** ↔ **Enthalpy** ↔ **Gibbs energy**

Ordering ↔ **Entropy**

$$\eta = Aexp(\frac{\Delta G^*}{RT})$$

$$\Delta G^* = \sum X_i \cdot \Delta G^*_i + \Delta G^*_{mix}$$

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$\Delta G = \sum X_i \cdot \Delta G_i + \Delta G_{mix}$$

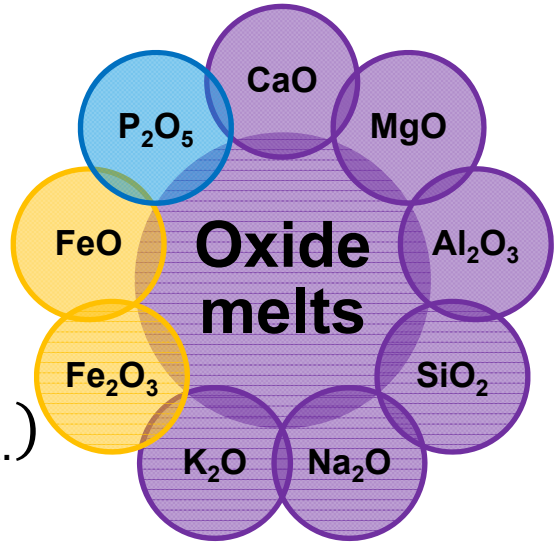
$$\left[\frac{d^2(\Delta G^*_{mix})}{dX^2}\right]_{P,T} = \left[\frac{d^2(\Delta G_{mix})}{dX^2}\right]_{P,T} - 6 \cdot R \cdot T$$

Viscosity model

JÜLICH FORSCHUNGSZENTRUM

Comp. Temp. → Associate species → Structure → Viscosity

Partial pressure of oxygen
(for FeO/Fe_2O_3-containing systems)



Modified Arrhenius model

$$\ln \eta = \ln \eta_{ideal} + \ln \eta_{excess}$$

$$= (\sum X_i \cdot \ln \eta_i) + (\ln \eta_{self-pol.} + \ln \eta_{inter-pol.})$$

where: $\ln \eta_i = A_i + B_i/T$ ⟶ basic structural units

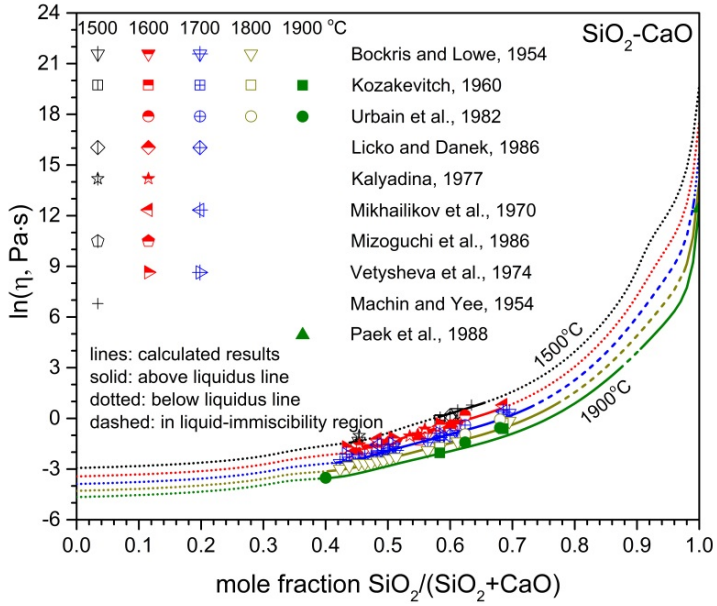
$$\ln \eta_{self-pol.} = \sum (A_{j,SiO_2} + B_{j,SiO_2}/T) \cdot (X^{n_j}_{SiO_2})$$

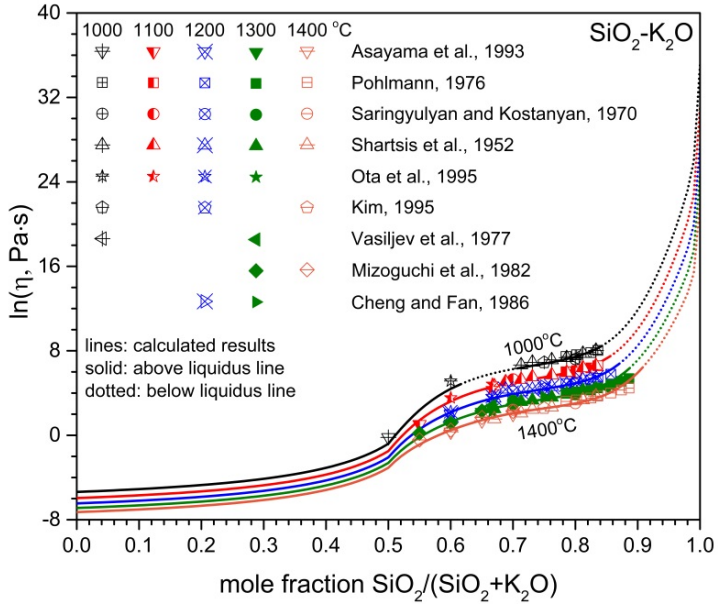
$$+ \sum_k (A_{(Si-Al)_k} + B_{(Si-Al)_k}/T) \cdot (X^{n_k}_{(Si-Al)_k})$$

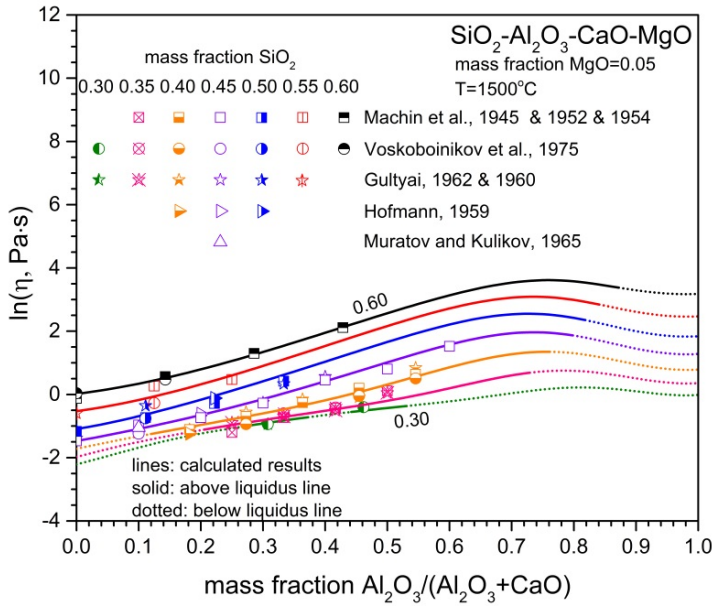
$$\ln \eta_{inter-pol.} = \sum_m (A_{(Si-Al)_m} + B_{(Si-Al)_m}/T) \cdot (X_{(Si-Al)_m} \cdot X^{n_m}_{SiO_2})$$

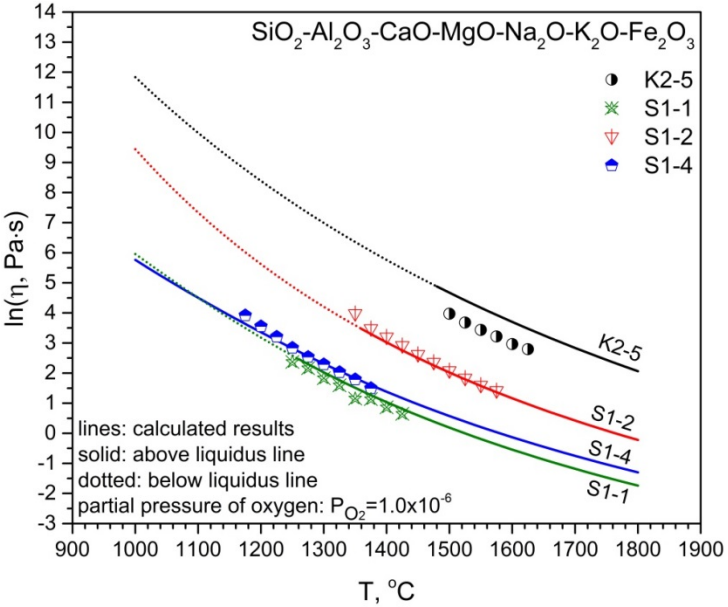
larger structural units

SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-FeO_x

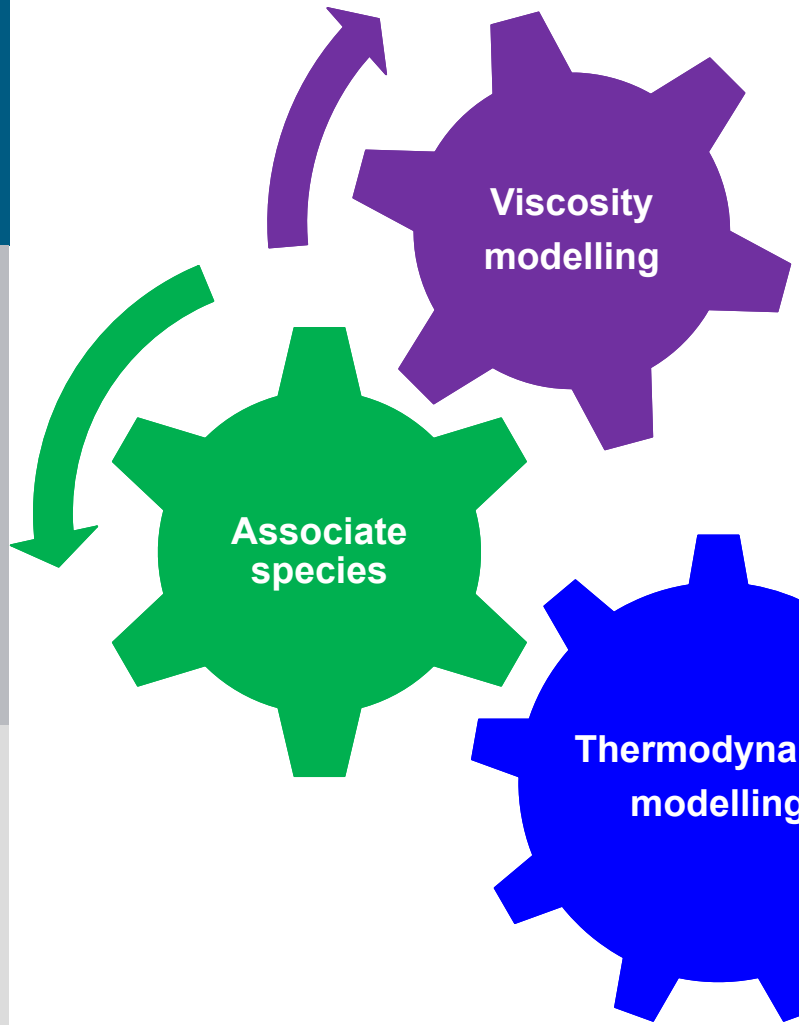


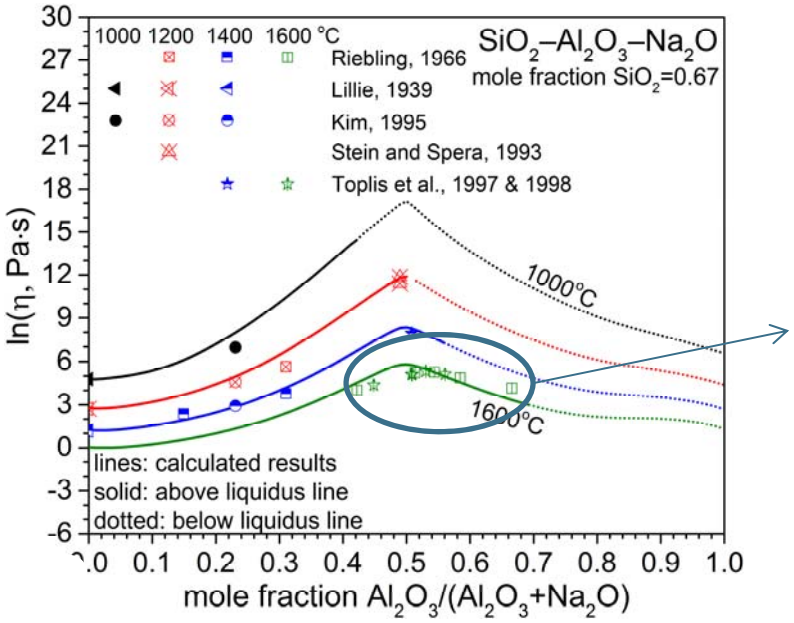




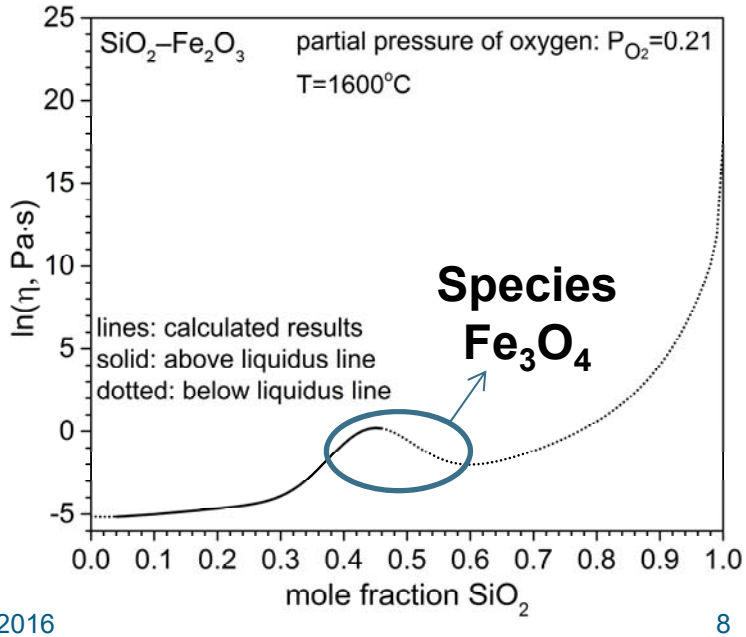


Feedback to thermodynamic database



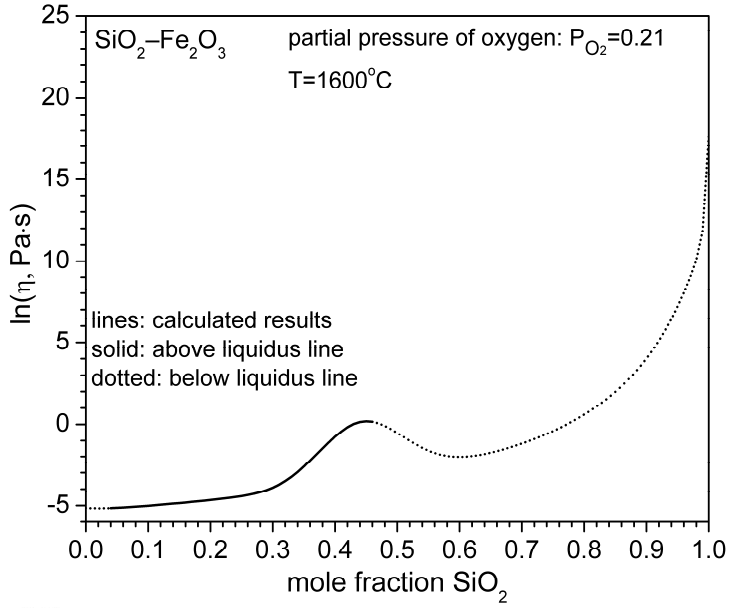


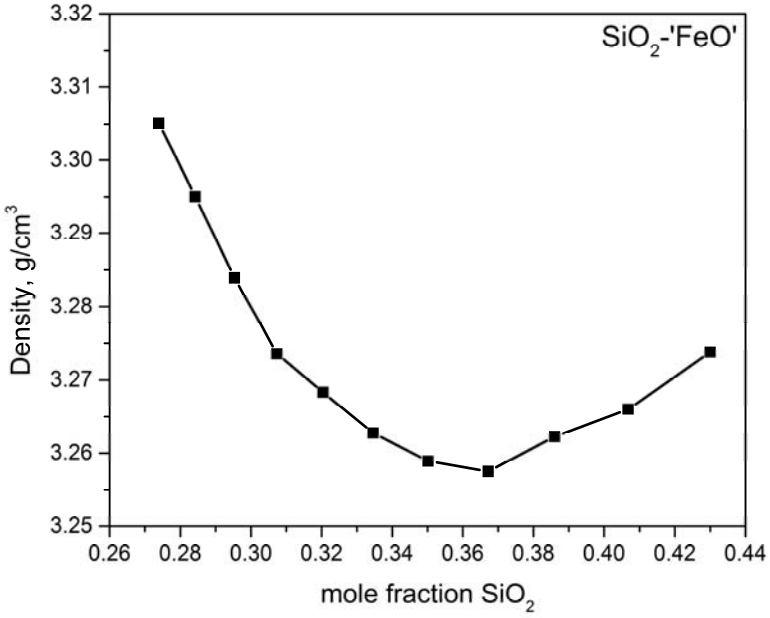
Tricluster species $AlSi_2O_{5.5}$

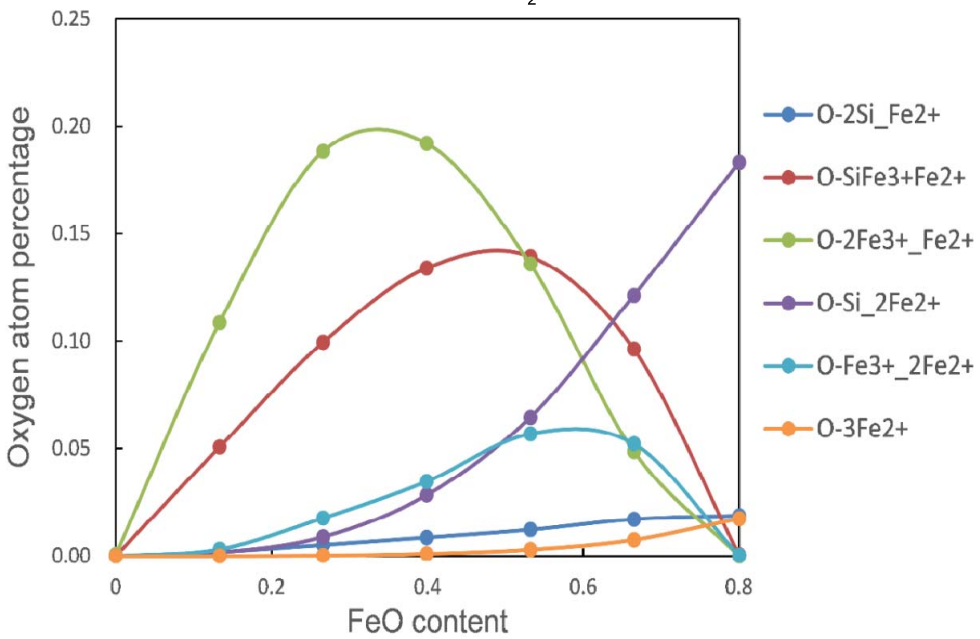


Species Fe_3O_4

FeO_x-containing sytems







Species
Fe_3O_4

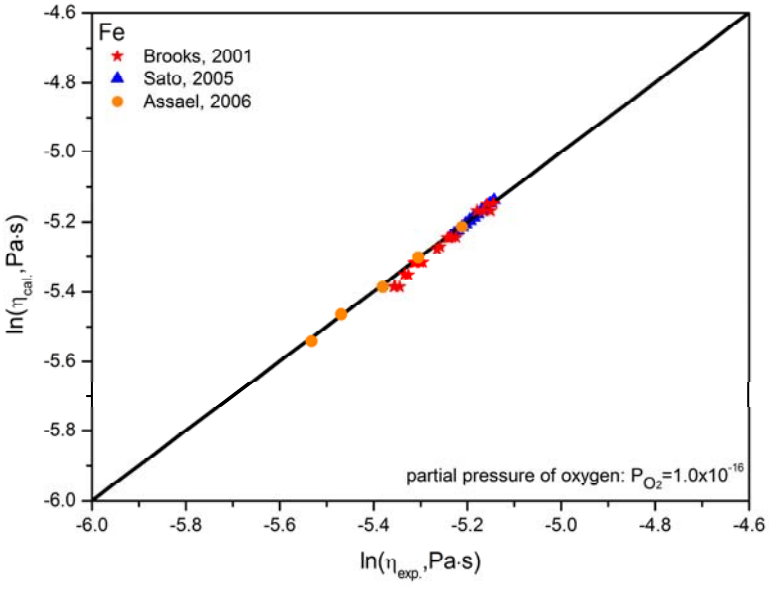
Species $SiFe_3O_6$:
$SiO_2 \cdot Fe_2O_3 \cdot FeO$

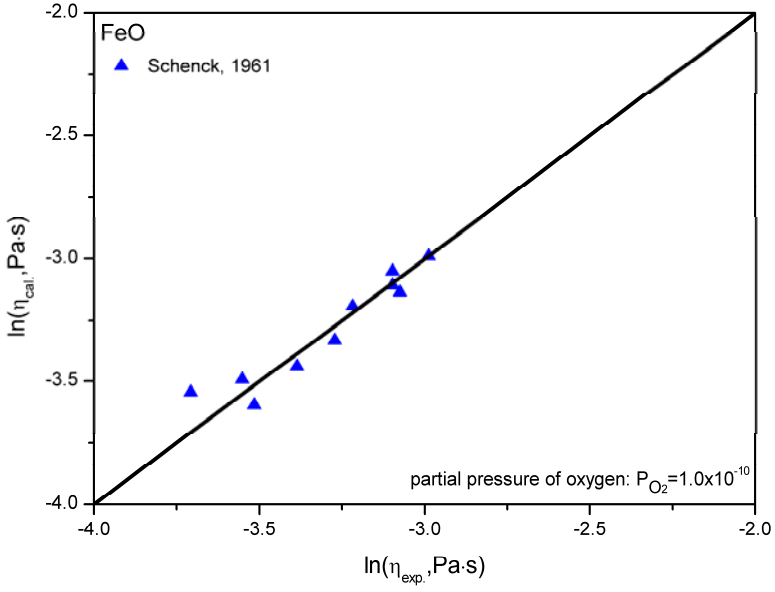
Parameters for FeO_x-containing systems

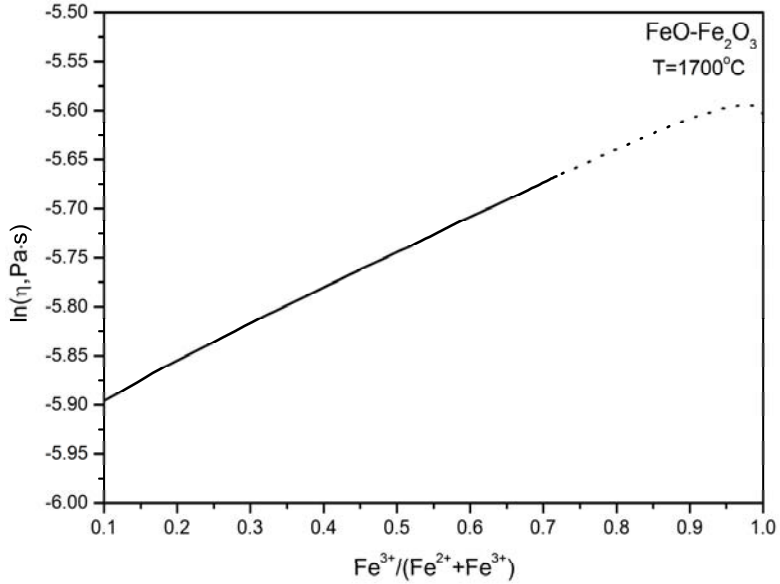
JÜLICH FORSCHUNGSZENTRUM

Structural unit i	Model parameters		Predicted theoretical viscosity and activation energy for viscous flow	
	A_i	B_i	$\eta_{T\to\infty}$, Pa·s	E_η, kJ/mol
Fe	–8.578	6.227	1.88×10^{-04}	51.77
FeO	–8.032	8.126	3.25×10^{-04}	67.56
Fe_2O_3	–11.241	11.135	1.31×10^{-05}	92.58
Fe_3O_4	–17.280	15.738	3.13×10^{-08}	130.85
$FeNa_2O_2$	–8.313	20.869	2.45×10^{-04}	173.52
$FeSiO_3$	–2.781	94.710	6.20×10^{-02}	787.46
Fe_2SiO_4	–25.356	23.339	9.72×10^{-12}	194.05
$FeSi_2CaO_6$	–17.375	18.347	2.85×10^{-08}	152.54
$FeSi_2MgO_6$	–41.444	39.274	1.00×10^{-18}	326.54
$FeSiNa_2O_4$	–2.971	10.773	5.13×10^{-02}	89.57
$FeAl_2O_4$	–18.848	26.008	6.53×10^{-09}	216.24
$Fe_2Si_5Al_4O_{18}$	–2.147	17.248	1.17×10^{-01}	143.41
$CaFe_2O_4$	–11.017	12.594	1.64×10^{-05}	104.71
$MgFe_2O_4$	–16.427	10.789	7.35×10^{-08}	89.70
$NaFeO_2$	–16.206	21.870	9.15×10^{-08}	181.84
$KFeO_2$	–10.310	23.560	3.33×10^{-05}	195.88

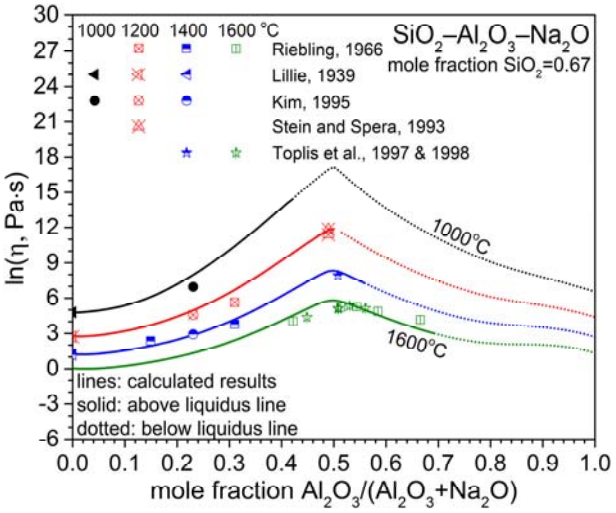
FeO_x-containing systems

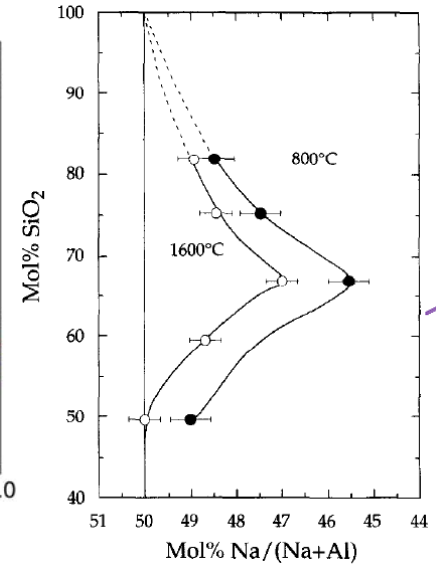


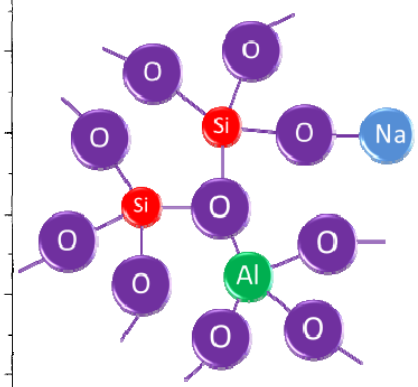




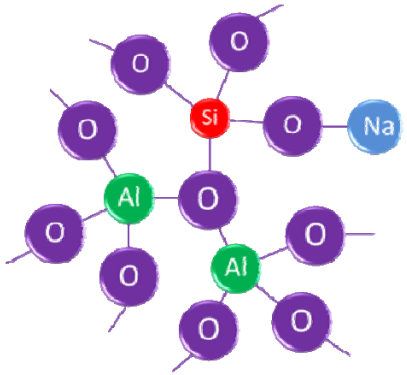
Shift of the viscosity maximum



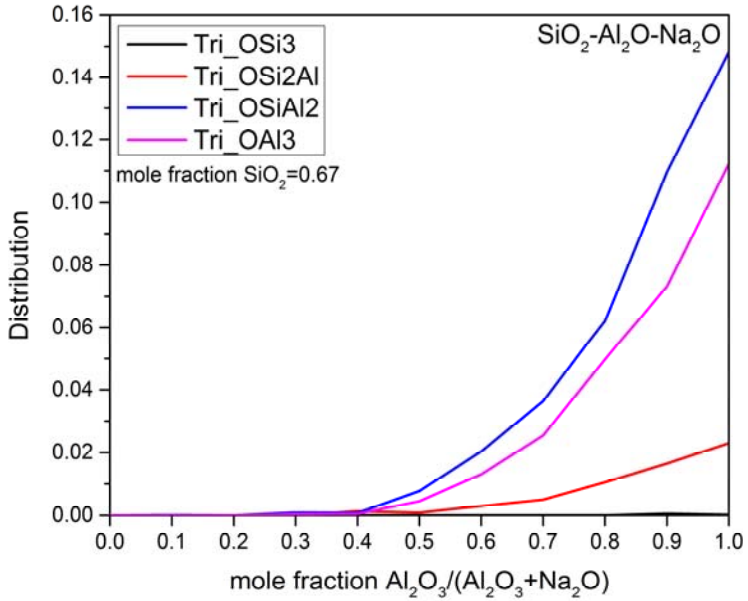


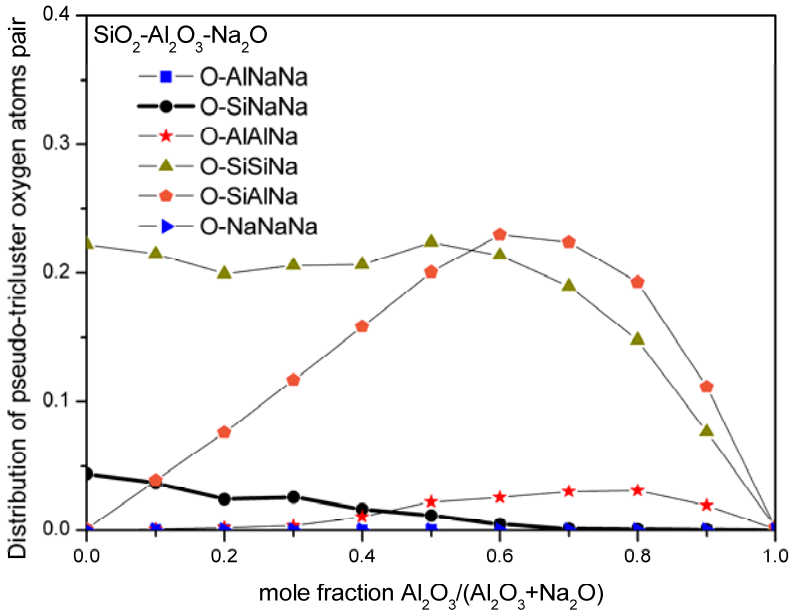


Tricluster species: $AlSi_2O_{5.5}$



Tricluster species: Al_2SiO_5

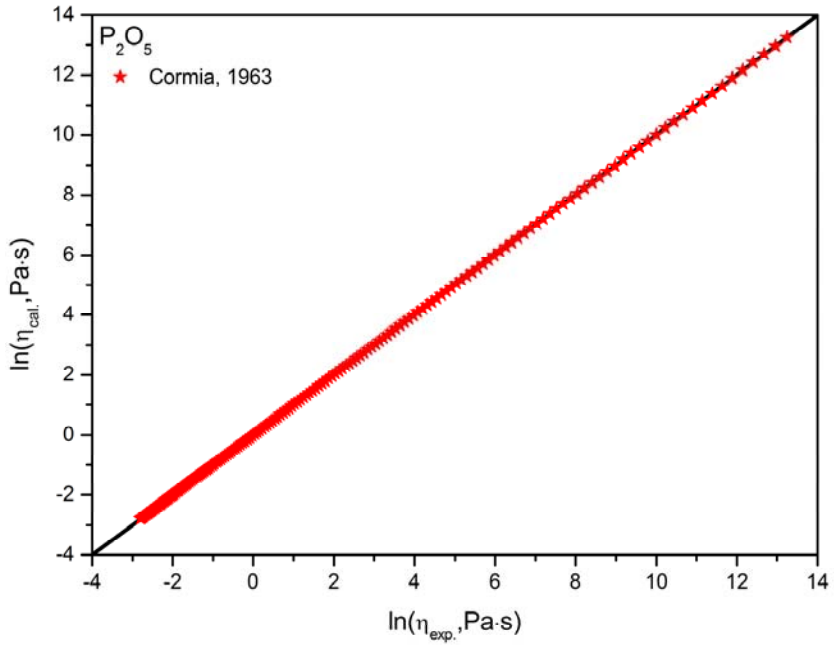




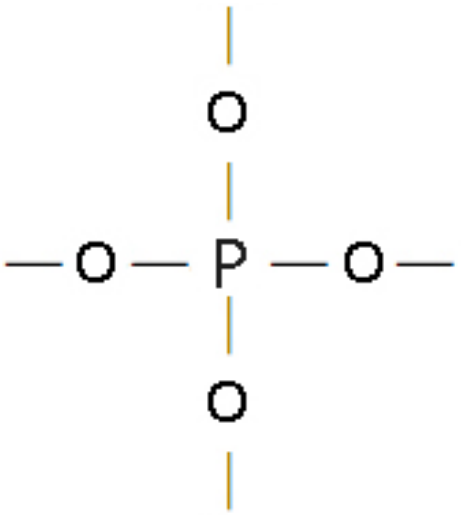
Associate species employed for P_2O_5-containing systems

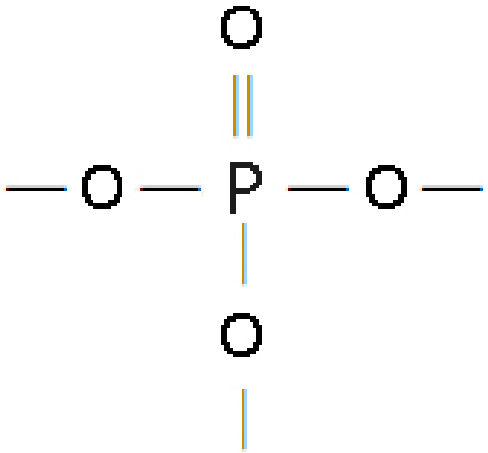
Associate species	Structural units	Associate species	Structural units
P_2O_5	$\mathbf{P}O_{2.5}$	$Na_4P_2O_7$	$Na_2\mathbf{P}O_{3.5}$
P_2SiO_7	$P_2\mathbf{Si}O_7$	$NaPO_3$	$Na\mathbf{P}O_3$
$P_4Si_3O_{16}$	$P_{4/3}\mathbf{Si}O_{16/3}$	Na_3PO_4	$Na_3\mathbf{P}O_4$
$AlPO_4$	$Al\mathbf{P}O_4$	KPO_3	$K\mathbf{P}O_3$
CaP_2O_6	$Ca_{0.5}\mathbf{P}O_3$	K_3PO_4	$K_3\mathbf{P}O_4$
$Ca_2P_2O_7$	$Ca\mathbf{P}O_{3.5}$	$K_4P_2O_7$	$K_2\mathbf{P}O_{3.5}$
$Ca_3P_2O_8$	$Ca_{1.5}\mathbf{P}O_4$	$FePO_4$	$Fe\mathbf{P}O_4$
$Mg_3P_2O_8$	$Mg_{1.5}\mathbf{P}O_4$	$Fe_2P_2O_7$	$Fe\mathbf{P}O_{3.5}$
$Mg_2P_2O_7$	$Mg\mathbf{P}O_{3.5}$	FeP_2O_6	$Fe_{0.5}\mathbf{P}O_3$
MgP_2O_6	$Mg_{0.5}\mathbf{P}O_3$	$Fe_3P_2O_8$	$Fe_{1.5}\mathbf{P}O_4$

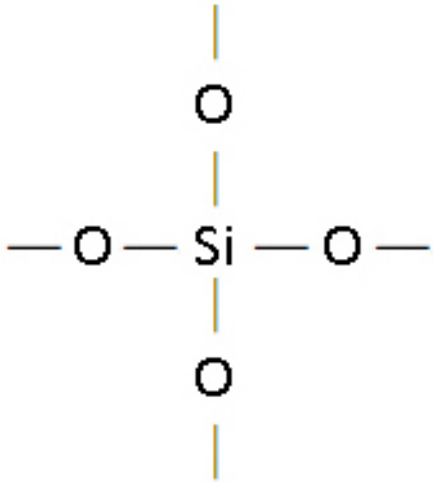
Pure oxide P_2O_5



Structural unit i	Model parameters	
	A_i	B_i
SiO_2	–11.841	26.008
P_2O_5	–16.720	20.884

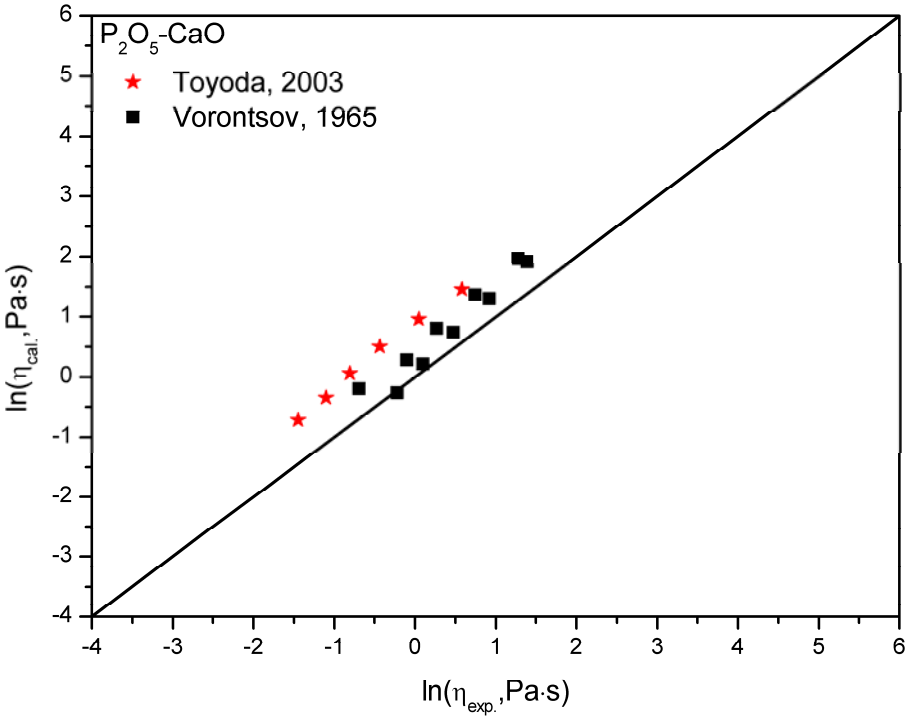


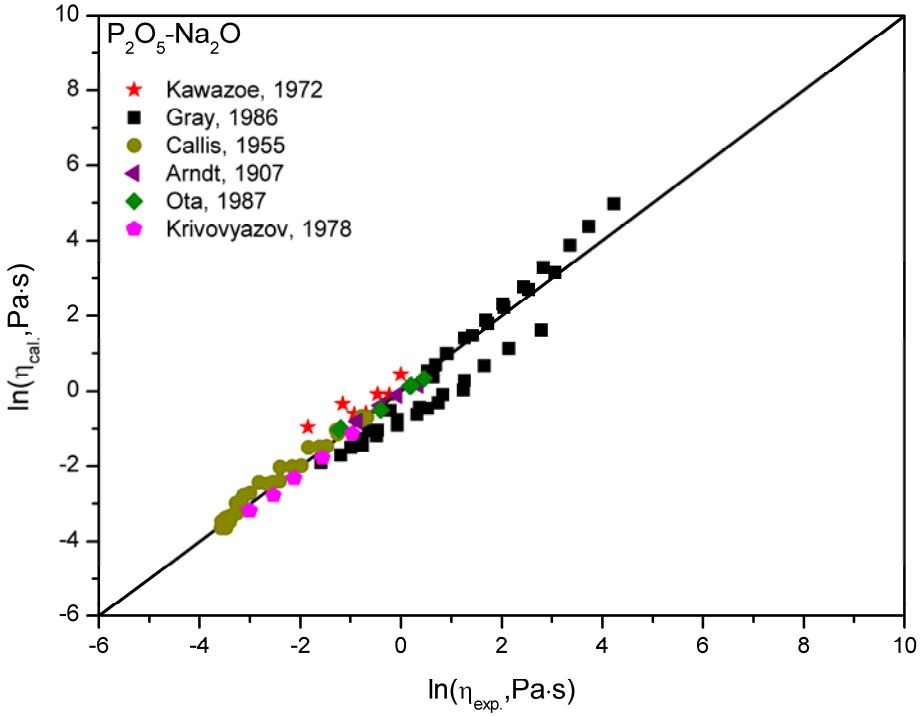




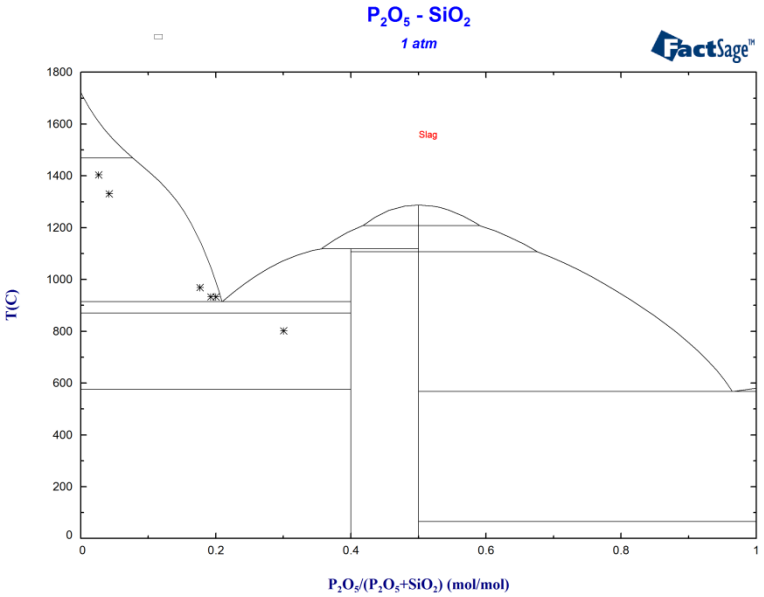
SiO_2
$(SiO_2)_6$
$(SiO_2)_{109}$

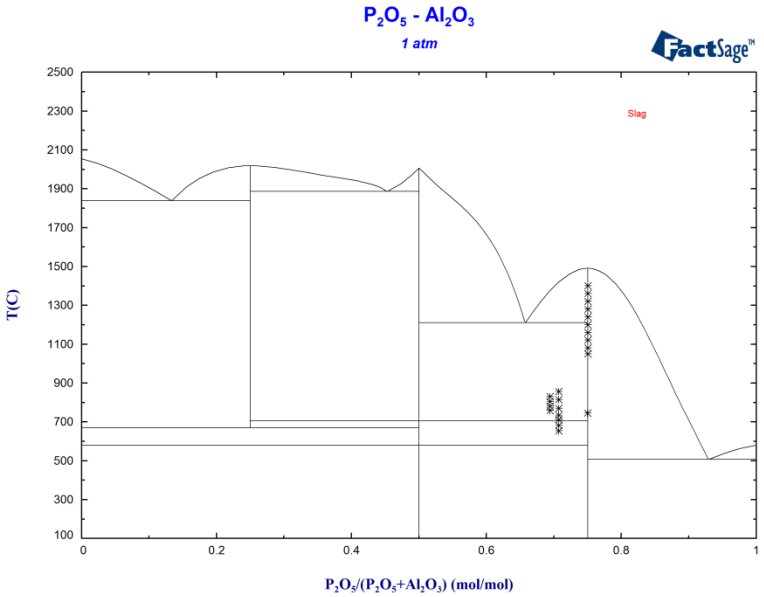
P_2O_5-containing binary systems

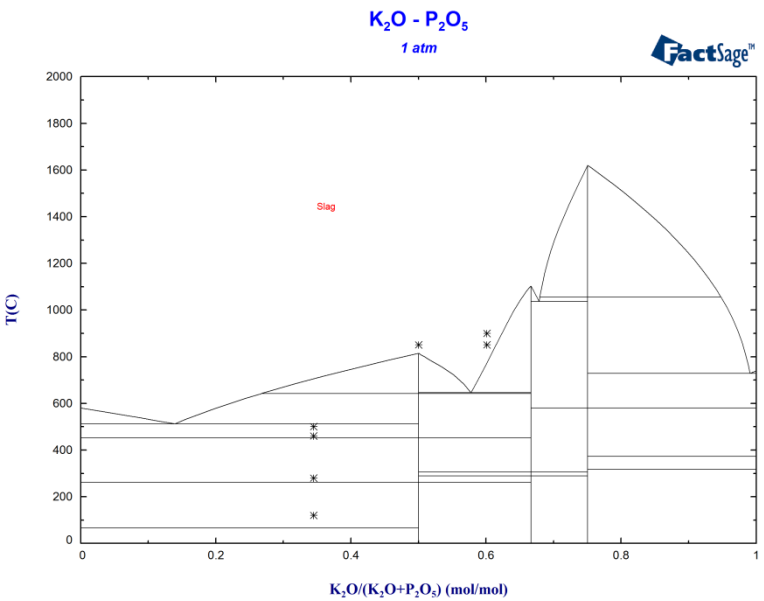


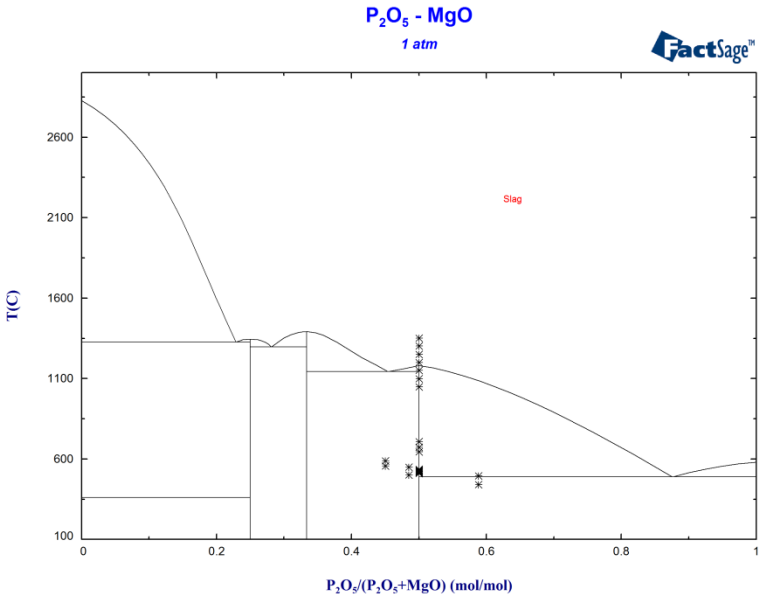


P_2O_5-containing binary systems

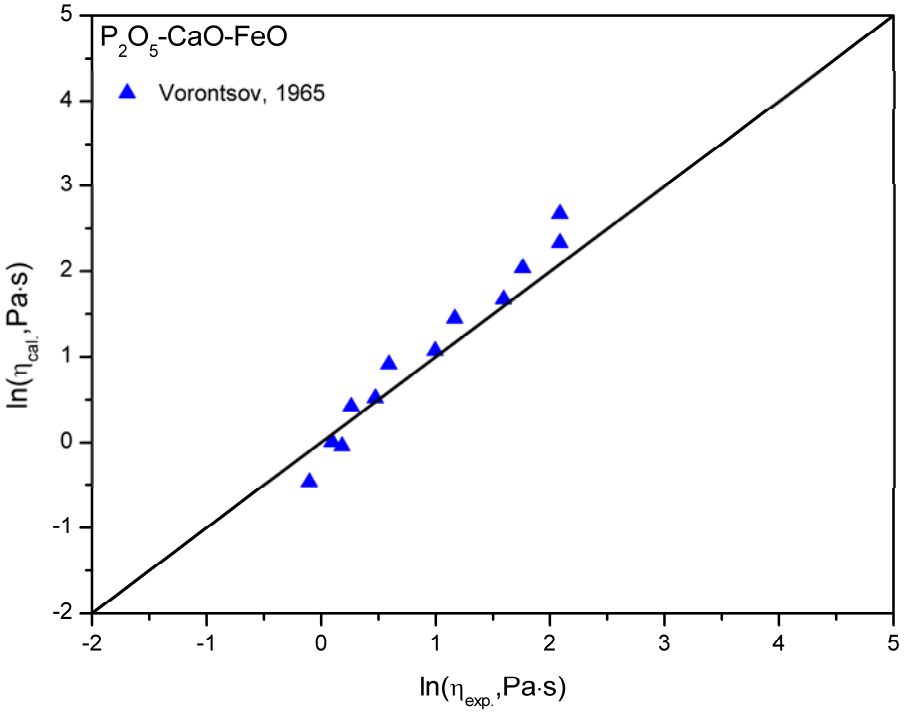




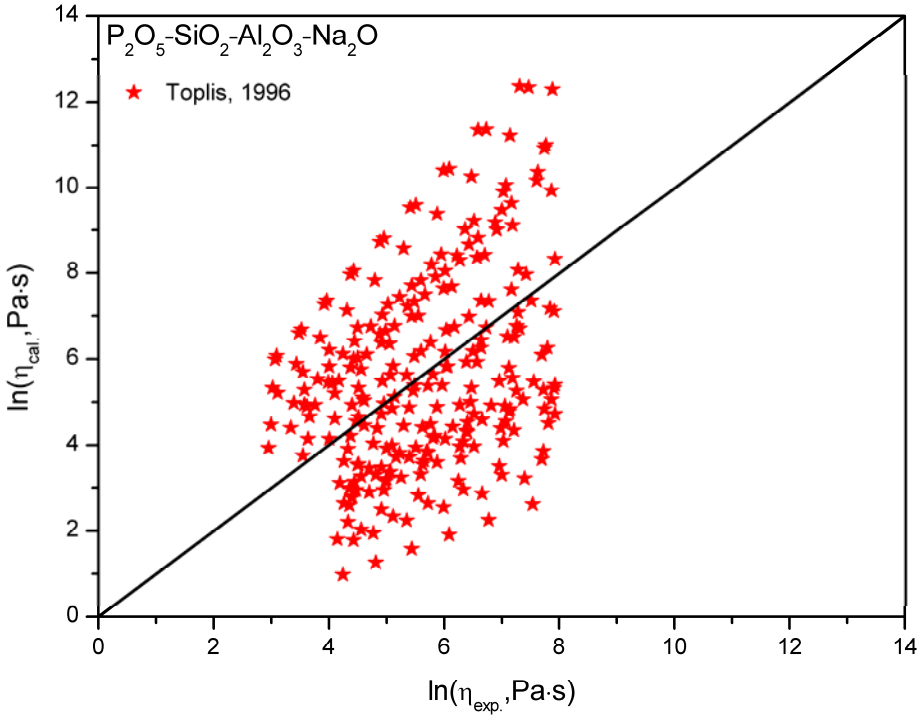




P_2O_5-containing higher order systems



P_2O_5 v.s. Al_2O_3



Outlook

- Describing challenging viscosity behaviors
  - The local viscosity maximum around fayalite compound in the binary system SiO_2-FeO_x
  - The shift of the viscosity peak in the ternary system SiO_2-Al_2O_3-Na_2O
- Performing MD simulations to obtain the structural information
- Accessing the model parameters for P_2O_5-containing systems
- Developing a stand-alone software to calculate viscosity
- Extending the model from fully molten slags to partly crystallized slags

Thank you very much for your attention!