A Vapor Pressure Model Including Group-Group Interactions: Impact on Secondary Organic Aerosol Yield

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Atmospheric Chemical Mechanisms, 10-12 December 2008, UCDavis 2008

Introduction: Boream model

- **B**iogenic **O**xidation and **RE**lated **A**erosol formation **M**odel
- Chemical mechanism to describe oxidation of α-pinene, coupled to an gas-to-particle partitioning module
- About 5000-10000 reactions and $>$ 1000 chemical species (depending on the version)
- Validation by comparing to smog chamber experiments
- *Capouet et al., J. Geophys. Res. 113, D02308 (2008)*

Outline

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Equilibrium limit: Pankow's formula

- Gas-to-particle partitioning is described kinetically.
- In the equilibrium limit, the following partitioning formula applies. $K_{p,i}$ =partitioning coefficient.

$$\frac{[\mathrm{A}_i(\mathrm{p})]}{[\mathrm{A}_i(\mathrm{g})]} = \frac{k_{\mathrm{on}}}{k_{\mathrm{off}}}[\mathrm{OA}] = \frac{RT}{p_i^0 \zeta_i N_{Avo}}[\mathrm{OA}]$$

$$= \frac{RT}{\overline{M}_{\mathrm{om}} p_i^0 \zeta_i N_{Avo}}[M_{\mathrm{OA}}] = K_{p,i}[M_{\mathrm{OA}}]$$

- This limit is reached in most simulations of smog chamber experiments.
- Higher [OA] leads to more condensation.
- Parameterizations have to be made for vapor pressure p_i^0 and activity coefficient ζ_i.
- Activity coefficient is calculated with a version of UNIFAC

Outline

Vapor pressure: current formulation.

- Vapor pressure formula (*Capouet et al. ACP (2006)*):

$$\log_{10} p_i^0 = \log_{10} p_{i,hc}^0 + \sum_k \nu_{i,k} \tau_k$$

  - $p_{i,hc}^0$: vapor pressure of the parent hydrocarbon: replace all the hetero-atoms by the appropriate amount of hydrogens.
  - $\tau_k = A + B \times (T - 298\mathrm{K})$: contribution of functional groups

Group parameterizations

	A	B		A	B
τ_{carb}	-0.8937	0.0039	τ_{COOH}	-3.2516	0.0075
τ_{ONO2p}	-2.0897	0.0063	τ_{OHp}	-2.6738	0.0171
τ_{ONO2s}	-1.6711	0.0063	τ_{OHs}	-2.0374	0.0124
τ_{ONO2t}	-1.2793	0.0063	τ_{OHt}	-1.4418	0.0103
τ_{OOH}	-2.9942	0.0361	τ_{PAN}	-3.0372	0.0133

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Shortcomings vapor pressure model

- No group-group interactions, both inter- and intramolecular.
- No carbon skeleton structural effects
- Parameters should be updated with newly available vapor pressure data.

Outline

Improvements in vapor pressure model

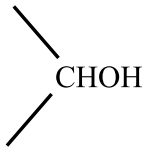
- More data included: about 460 molecules
  - Direct vapor pressure data where possible. Mono- and bifunctional compounds.
  - When necessary: estimation from experimental boiling point. (*Moller et al., J. Mol. Liq. 2008*).
  - Gas chromatography data: useful for relative trends within one class of molecules.
- Model includes:
  1. Functional groups: -C(=O)-, -COOH, -OH, . . .
  2. Carbon skeleton effects: -$CH(CH_3)COOH$ vs. -CH_2COOH,. . .
  3. Neighbour (intramolecular) group-group interactions: -C(=O)COOH, -C(=O)C(=O)-,. . .
  4. Long range (intermolecular) group-group interactions: $HOCH_2 \ldots CH_2OH$, $HOCH_2 \ldots CH_2COOH$,. . .

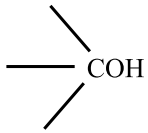
Functional groups: -C(=O)OX

- These lower the vapor pressure by about three orders of magnitude.

	$\tau(298K)$
-C(=O)OH	-3.45
-C(=O)OOH	-2.85
-C(=O)OONO_2 (PAN)	-3.04

Functional groups: effect of placement

- For ring or chain, a functional group lowers the vapor pressure more in the order primary -CH_2OH> secondary 

> tertiary 

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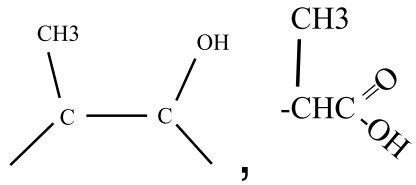
- A functional group in a ring lowers the vapor pressure more than in a chain

	p	sc	s	tc	t
OH	-2.27	-2.09	-1.68	-1.65	-1.35
ONO_2	-2.33	-2.24	-1.89	-2.01*	-1.85
OOH	-3.15	-3.65	-2.85*	-3.43*	-2.69
C=O	-1.2 (aldehyde)	-1.36	-1.1	x	x

*Estimated by analogy with other groups.

Carbon skeleton effects

- A carbon on the 2-position increases the vapor pressure.
  - e.g. 

  ,
  - This effect is much more important in a ring than in a chain.
- A double bond in combination with a carbonyl or acid lowers the vapor pressure.

chain		ring		alkene with	
C next to		C next to			
-CH_2OH	+0.07	OHsc	+0.57	C=O	-0.31
-CH_2ONO_2	+0.14	C=O	+0.3 (CH_3)	COOH	-0.10
C=O	+0.08		+0.5 (C_2)		
-COOH	+0.25				

- Similar parameters for C(=O)OOH, OOH, etc. can be estimated by analogy.

Neighbouring functional groups (intramolecular interaction)

- Compared to similar molecules with non-neighbouring groups, the vapor pressure is increased.
- Effect in a ring is in general stronger than in a chain.
- Important for carbonyl in conjugation with carbonyl or acid

chain		ring	
OH,OH	+0.33	OH,OH	+0.94
C=O,C=O	+0.90	C=O,C=O	+0.47
ONO_2,ONO_2	+0.21	ONO_2,ONO_2	+0.44
OH,ONO_2	+0.02	OH,ONO_2	+0.28
OH,C=O	+0.22		
C=O,COOH*	+1.82		
OH,COOH*	+1.98		

* Based on limited and/or scattered data.

Long range (intermolecular) interaction

- Especially important between groups that do hydrogen-bonding. These interactions lower the vapor pressure.

	OH	CO	COOH
OH	-0.83	0.*	-1.59*
CO		0.08	-1.0*
COOH			-1.25*

* Based on limited and/or scattered data

Summary

- Vapor pressure model can be improved by including interactions between groups.
  - This lowers the vapor pressure especially for molecules with several hydrogen-bonding groups
- For several interaction terms, there is a lack of data and their contributions have to be estimated or neglected. More experimental data would be greatly appreciated!

Outlook

- With the (limited) data available on molecules with more than 2 functional groups, look what is the best method for 'counting' group-group interactions.
- Maybe devise an activity coefficient method based on similar principles, to have a more unified approach.