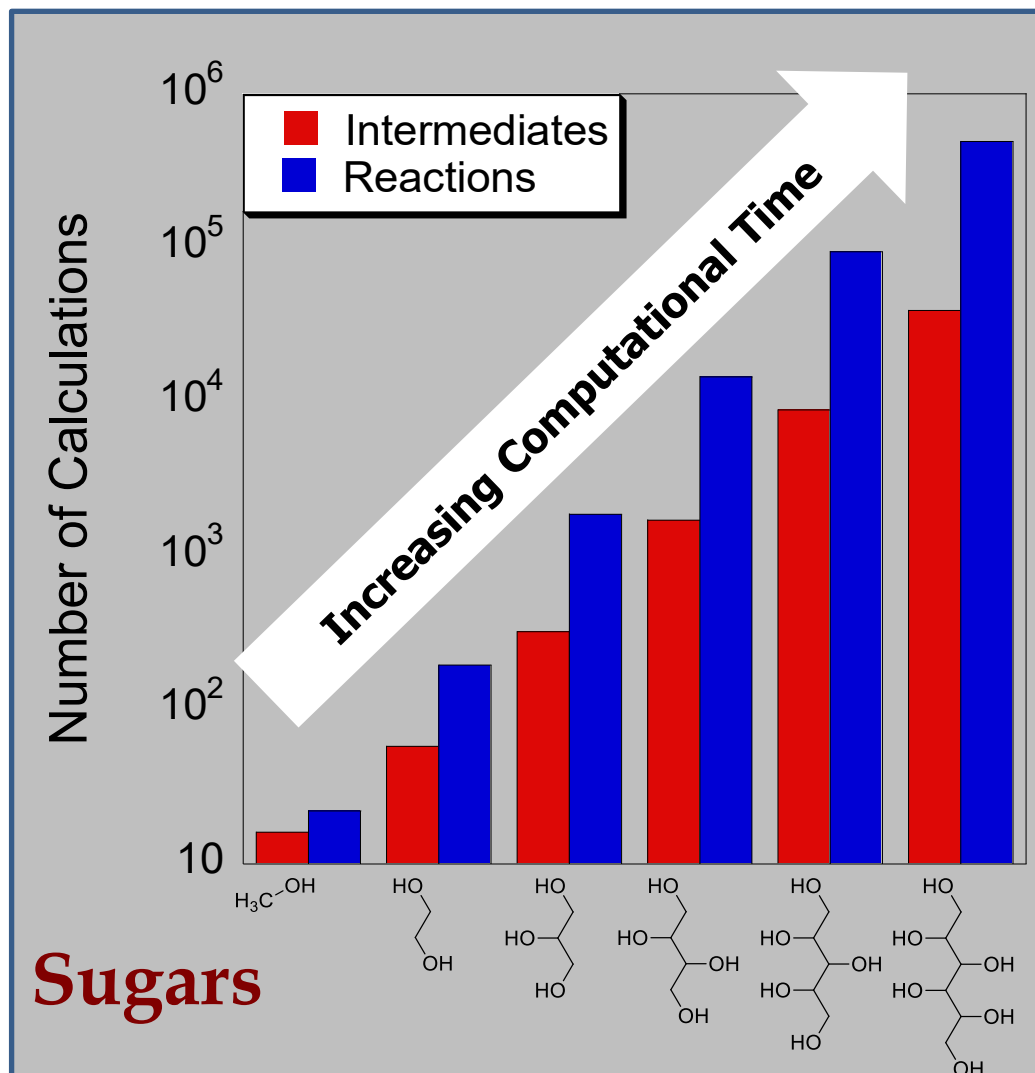


Theory, Applications, and Tools for Multiscale Kinetic Modeling: Parameterizing Large Models

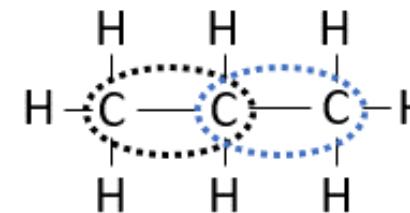
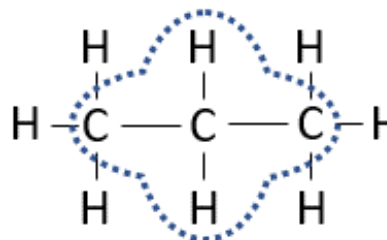
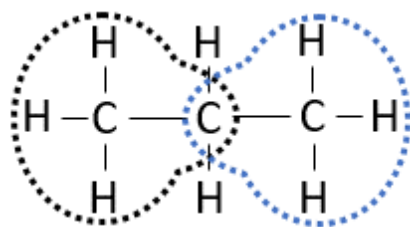
D. Vlachos and G. R. Wittreich

Modeling Reactions of Large Molecules is Challenging



- Combinatorial explosion in number of calculations for first-principles (DFT) calculations
- Semi-empirical methods can potentially parametrize relevant species and reactions instantaneously
- Major advances in systematic development of semi-empirical methods and understanding of errors

Method: Group Additivity^{1,2}



Propane (C_p , H , S) = $2 \times \mathbf{C(C)(H)_3}$ + $1 \times \mathbf{C(C)_2(H)}$ + $2 \times \mathbf{CC}$

Training Molecules	Groups															
	2	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0
	1	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0
	2	0	0	0	1	0	0	0	0	0	0	1	0	0	0	0
	0	0	0	0	2	0	0	0	0	0	1	0	0	0	2	0
	0	0	0	2	0	0	0	0	0	2	0	0	1	0	0	0
	0	0	2	2	0	0	1	0	0	1	0	2	2	0	0	0
	1	1	0	0	0	0	0	0	1	0	0	1	0	0	0	0
	0	1	0	0	0	0	0	0	2	1	0	0	0	0	0	0
	2	2	2	0	0	0	2	0	0	0	1	1	0	0	0	0
	2	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0
	2	1	0	0	0	0	0	0	1	0	2	0	0	0	0	0
	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	1

$\mathbf{X}_{T[m \times g]}$

•

Thermodynamic Property (Group)	

$\beta_{[g \times 1]}$

=

Thermodynamic Property (Molecule)	

$Y_{T[m \times 1]}$

$$\beta_{[g \times 1]} = \mathbf{X}_{T[m \times g]}^+ \cdot Y_{T[m \times 1]}$$

$$\beta_{[g \times 1]} = \left(\mathbf{X}_{T[g \times m]}' \cdot \mathbf{X}_{T[m \times g]} \right)^{-1} \cdot \mathbf{X}_{T[g \times m]}' \cdot Y_{T[m \times 1]}$$

$$\hat{\sigma} = \sqrt{\frac{\sum \left(\mathbf{X}_{T[m \times g]} \cdot \beta_{[g \times 1]} - Y_{T[m \times 1]} \right)^2}{m - g}}$$

$$\hat{\sigma}_{C_p} = 0.12 - 0.73 \text{ cal/mol} \cdot K$$

$$\hat{\sigma}_H = 4.53 \text{ kcal/mol}$$

$$\hat{\sigma}_S = 2.07 \text{ cal/mol} \cdot K$$

 GrAdd³

¹ Benson, S. W. et al. (1969), *Chemical Reviews*

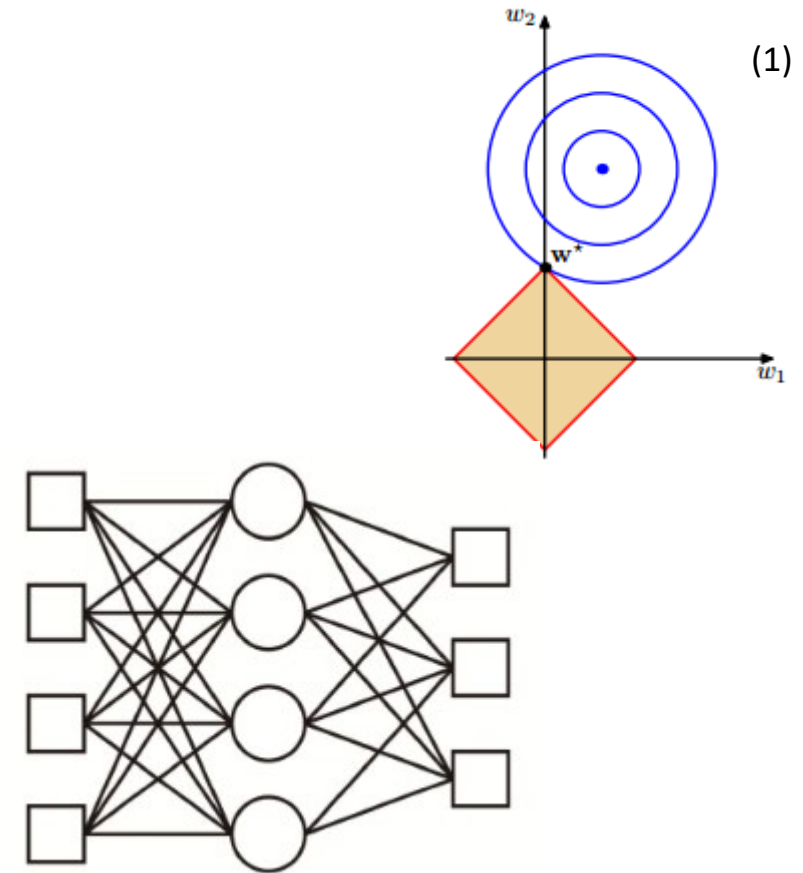
² Kua, J. and Goddard, W. A. (1998), *J. Phys. Chem. B*

³ <https://github.com/VlachosGroup/PythonGroupAdditivity>

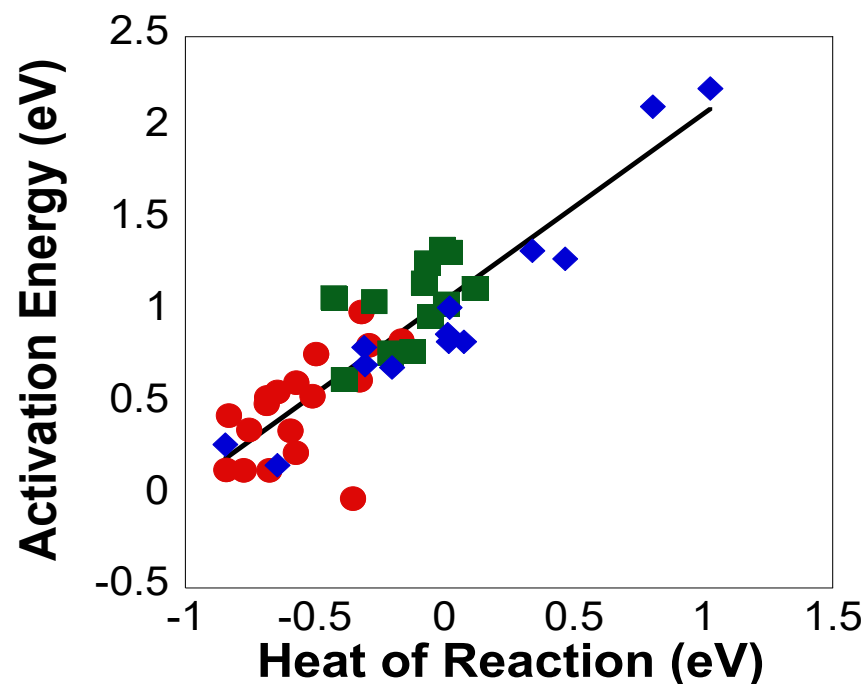
Gu et al. (2018), *Reaction Chemistry & Engineering*.

Method: Machine Learning

- Increasingly popular approach
- Not limited to a single scheme as group additivity
 - Groups may not be necessary
 - Groups, if used, are not limited to a single scheme
 - Not limited to linear relationships
 - More complex relationships can be explored
- Can achieve better fit with training data
- Can lose some of the physics



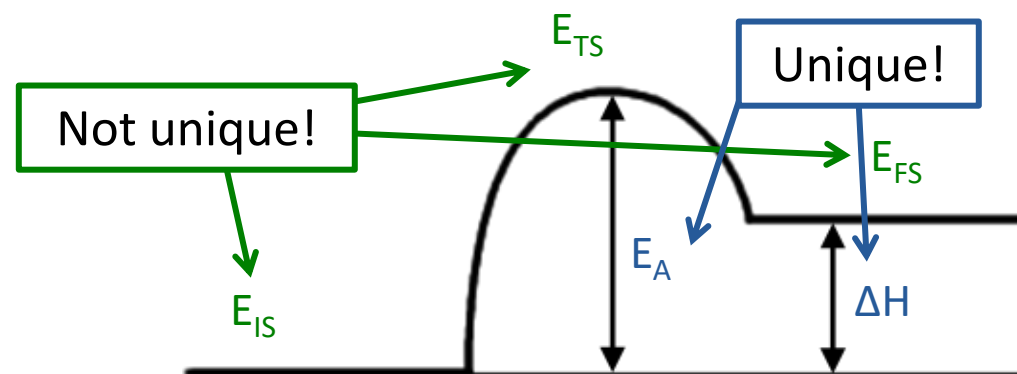
Brønsted-Evans-Polanyi (BEP) Relationships¹



$$\Delta E_{a,i} = \omega \Delta H_{rxn,i} + \Delta E_0$$

- BEP relationships can be used as they enable the prediction of reaction barriers from the heat of reactions for an entire homologous series of reactions
- BEPs for common homologous series are available

C—C
C—H
C—OH
C—O
O—H

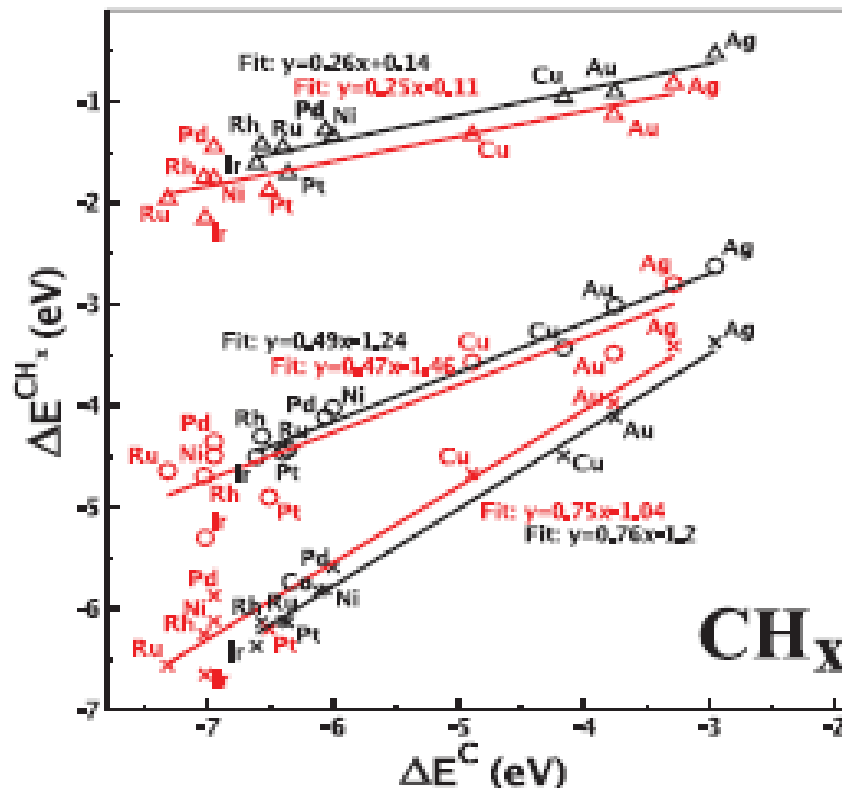


Linear Scaling Relationships (LSRs) for Metal Cats

$$Q^{AH_x} = \gamma Q^A + \beta, \quad \gamma = \frac{x_{\max} - x}{x_{\max}}$$

Simple/Small Molecules:
CH_x, NH_x, OH_x, SH_x,...

- They work well when AH_x binds on catalysts with the same binding mode, e.g., bridge binding
- **Impact:** By computing Q_A on a new catalyst, e.g., bimetallic, you can compute Q_{AH_x} , so one saves some comps



- Polyatomic/Multidentate Adsorption: Extended LSR

$$Q_{i,new} = Q_{i,ref} + \sum_{j=1}^n \gamma_{i,j} \left(Q_{new}^{ref\ species, j} - Q_{ref}^{ref\ species, j} \right)$$

Summary of Semi-empirical Methods

- Group additivity estimates species thermochemistry for large molecules and mechanisms
 - Once the groups have been identified via graph theory and the values estimated, these can be used for any mechanism on the same catalyst
 - Reaction thermochemistry is estimated from species thermochemistry
- Extended linear scaling relations can be used to estimate species thermochemistry on a new catalyst from a reference catalyst
- BEPs or transition state scalings can be used to estimate reaction barriers from thermochemistry
 - BEP is applied to the entire homologous series; a few DFT data to estimate and information is then transferable to all reactions of the same family
 - Tacitly assumed that the BEP holds among catalysts for the same chemistry
- These relations are linear; machine learning can be used to improve accuracy, identify descriptors, e.g., groups in GA, and capture nonlinear effects