

# Summary of Part 1: Overview, Chem Basics

- Fuels are both Boon and Bane
  - Oil: cheap-to-produce convenient high-density energy carrier
  - Current system not sustainable, esp. greenhouse
  - So we need: 1) higher efficiency 2) new energy carrier
    - Maybe an Alternative Fuel?
    - If so, need to understand how it behaves...
- Fuel Chemistry is Tricky
  - NOT Arrhenius single step!!
  - Details matter to understand why fuels behave differently
- Many clever (tricky) methods for experimentally measuring rates...but you cannot measure everything
- ...Most of the rest of the lectures focus on understanding fuel chemistry theoretically / computationally

# Combustion Chemistry, Part 2

# Plan of attack

- start with Thermodynamics/Thermochemistry
  - Including equilibrium Statistical Mechanics
- Next simple Rate Theory
  - conventional Transition State Theory
  - high- $P$ -limit (thermalized)
- Then Fancier Rate Theory
  - variational TST
  - $P$ -dependence of rate coefficients
- Then Mechanisms combining many species, reactions

# Thermodynamics/Thermochemistry

All Kinetics is Leading Toward Equilibrium. So good to start by figuring out where we are going (later we can worry about how fast we will get there...)

Part of Thermo is about phase behaviour (e.g. volatility, miscibility)

“Thermochemistry” is about reactions.

1<sup>st</sup> Law gives energy density, final temperature

2<sup>nd</sup> Law related to detailed balance (and so reverse rate coefficients), final composition at equilibrium

Fuel volatility must match fuel injector, and certain volatility ranges are particularly hazardous to store.  
Gasoline boils  $\sim 150\text{ C}$ , jet  $\sim 200\text{ C}$ , diesel  $\sim 300\text{ C}$

Large molecules pyrolyze at lower T than b.p., and are solids at room temperature.

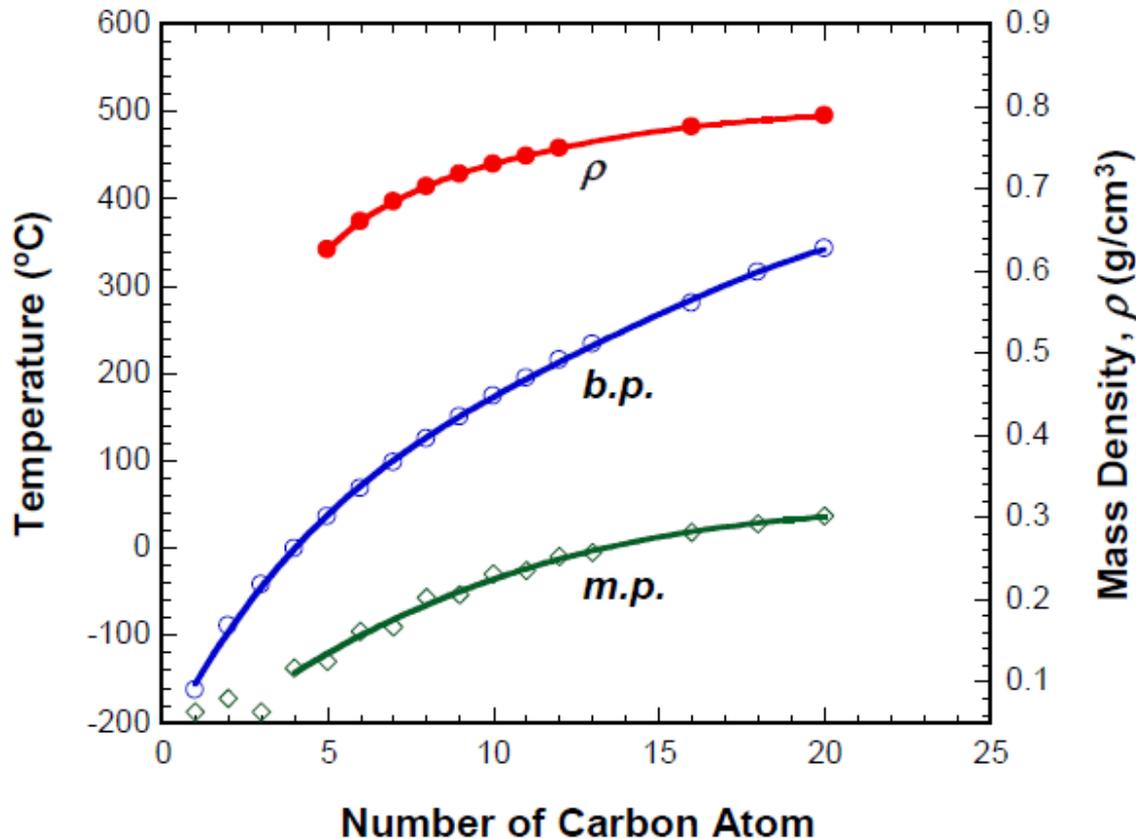


Figure 2.6 Variation of normal boiling and melting points (1.015 Bar) and liquid mass density of straight chain alkanes.

# Volatility, Solvation

- Phase behavior of mixtures is complicated subject in itself
  - How liquid fuel evaporates in engine
  - Formation of aerosols in atmosphere (particulate pollution)
  - Distillation is main separation process in refinery
  - Some liquids are immiscible, so can have several liquid phases
    - Don't want this to occur in fuel tank or fuel injector!
    - Strongly affects mobility in environment
- Volatility (Partial Pressure of species in gas phase) depends on solvation of the molecule in the liquid phase
  - Non-bonded interactions (Enthalpic interactions)
  - Entropy of molecule in liquid (mostly hard-sphere)
- Boiling Point is just when sum of all the partial pressures equals atmospheric pressure. Pure-compound boiling point not directly related to Henry's Law constant when species is in solution

# Thermodynamics

- We need thermodynamic data to:
  - Determine the heat release in a combustion process (need enthalpies and heat capacities)
  - Calculate the equilibrium constant for a reaction - this allows us to relate the rate coefficients for forward and reverse reactions (need enthalpies, entropies (and hence Gibbs energies, and heat capacities).
- This lecture considers:
  - Classical thermodynamics and statistical mechanics - relationships for thermodynamic quantities
  - Sources of thermodynamic data
  - Measurement of enthalpies of formation for radicals
  - Active Thermochemical Tables
  - Representation of thermodynamic data for combustion models

Various thermodynamic relations are needed to determine heat release and the relations between forward and reverse rate coefficients

at constant  $p$ ,  $\Delta H = \Delta U + p\Delta V$

$$\Delta_r H = \sum_{\text{products}} v_i \Delta_f H_i - \sum_{\text{reactants}} v_i \Delta_f H_i$$

A statement of Hess's Law

$v_i$  is the stoichiometric coefficient

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \sum_i v_i C_{p,i} dt$$

at constant  $T$ ,  $\Delta G = \Delta H - T\Delta S$

$$RT \ln K = -\Delta G$$

$$K = \frac{\prod_{\text{products}} (a_i^{v_i})}{\prod_{\text{reactants}} (a_i^{v_i})}$$

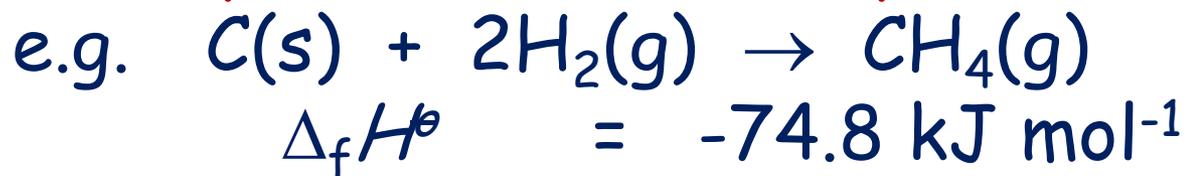
For ideal gas or ideal solution,  $a_i = P_i/P^\circ$  or  $a_i = C_i/C^\circ$ . Must use same standard state used when computing  $\Delta G^\circ$ . Solids have  $a_i=1$ . For surface sites use fractional occupation.

# Tabulated thermodynamic quantities.

## 1. Standard enthalpy of formation

### Standard enthalpy change of formation, $\Delta_f H^\ominus$

The standard enthalpy change when 1 mol of a substance is formed from its elements in their reference states, at a stated temperature (usually 298 K). The reference state is the most stable state at that temperature, and at a pressure of 1 bar.



The standard enthalpies of formation of  $C(s)$  and  $H_2(g)$  are both zero

## Computing $K_{eq}(T)$ , $G(T)$ , $H(T)$ , $S(T)$

$$H^0(T) = U + PV = H^0(T^0) + \int_{T^0}^T C_p(T') dT'$$

$$S^0(T) = S^0(T^0) + \int_{T^0}^T (C_p(T')/T') dT'$$

$$G^0(T) = H^0(T) - TS^0(T)$$

$$K_{eq}(T) = \exp(-G^0(T))$$

None of these depend on Pressure (they are for standard state)

Same  $K_{eq}$  works at all pressures. For non-ideal gases, the non-idealities are conventionally hidden in the activities as Fugacities or “activity coefficients”.

$C_p(T)$  is expressed in several different formats causing some confusion: NIST/Benson tabulated  $C_p(T_i)$  or several different polynomial-type expansions: Shomate, Wilhoit (beware typos in original paper), two different NASA formats.  $C_p(T)$  can also be expressed by statistical mechanics formulas.

Species	$\bar{h}_f^\circ(298\text{K})$	$\bar{s}^\circ(298\text{K})$	$\bar{c}_p(T)$ (J/mol-K)					
	(kJ/mol)	(J/mol-K)	298	500	1000	1500	2000	2500
C(S)	0	5.730	8.523	14.596	21.624	23.857	25.167	25.976
H <sub>2</sub>	0	130.663	28.834	29.297	30.163	32.358	34.194	35.737
O <sub>2</sub>	0	205.127	29.377	31.082	34.881	36.505	37.855	38.999
H <sub>2</sub> O	-241.8	188.810	33.587	35.214	41.294	47.333	51.678	54.731
CO	-110.5	197.640	29.140	29.811	33.163	35.132	36.288	36.917
CO <sub>2</sub>	-393.5	213.766	37.128	44.628	54.322	58.222	60.462	61.640
CH <sub>4</sub>	-74.6	186.351	35.685	46.494	73.616	90.413	100.435	106.864
C <sub>2</sub> H <sub>6</sub>	-83.9	229.051	52.376	77.837	122.540	144.761	158.280	165.774
C <sub>3</sub> H <sub>8</sub>	-103.8	270.141	73.530	112.409	174.614	204.334	222.359	232.305
C <sub>4</sub> H <sub>10</sub>	-125.8	309.686	98.571	148.552	227.379	264.424	286.823	299.106
C <sub>8</sub> H <sub>18</sub>	-208.7	466.772	187.486	286.282	431.399	494.910	534.404	557.447
C <sub>2</sub> H <sub>4</sub>	52.3	219.156	42.783	62.321	93.860	109.190	118.563	123.799
C <sub>2</sub> H <sub>2</sub>	227.4	200.892	43.989	54.715	67.908	75.906	81.045	84.262
CH <sub>3</sub> OH	-200.9	239.785	44.030	59.526	89.656	105.425	113.891	118.560
C <sub>6</sub> H <sub>6</sub>	82.8	269.020	82.077	138.240	210.948	240.242	257.667	267.023
H•	218.0	114.706	20.786	20.786	20.786	20.786	20.786	20.786
O•	249.2	161.047	21.912	21.247	20.924	20.846	20.826	20.853
OH•	39.3	183.722	29.887	29.483	30.694	32.948	34.755	36.077

The thermochemical data of a large number of species has been compiled by the National Institute of Standards and Technology. These data may be found at <http://webbook.nist.gov/chemistry/>. Another web-based source of data is the Active Tables (ATcT): [https://cmcs.ca.sandia.gov/cmcs/portal/user/anon/js\\_pane](https://cmcs.ca.sandia.gov/cmcs/portal/user/anon/js_pane).

For combustion calculations, a very good source of thermochemical data is: Alexander Burcat and Branko Ruscic “Third Millennium Thermodynamic Database for Combustion and Air-Pollution Use,” 2005 (<http://www.technion.ac.il/~aer0201/> or <http://garfield.chem.elte.hu/Burcat/burcat.html>). **Now maintained by Elke Goos.**

The database is the result of extensive work by Professor Alexander Burcat of Technion University, Israel over the last 20 years. In this database, the thermochemical data are expressed in the form of polynomial function and are thus more compact than the JANAF table. A typical record of thermochemical data may look like the following:

Species name	Reference source	Composition	Phase	$T_{Low}, T_{high}, T_{mid}$	
CO2	L 7/88C	10 2 0 0G	200.000	6000.000 1000.	1
$a_i (i = 1,7) \text{ for } T_{mid} < T < T_{high}$					2
$a_i (i = 1,7) \text{ for } T_{low} < T < T_{mid}$					3
$a_i (i = 1,7) \text{ for } T_{mid} < T < T_{high}$					4

$$\bar{c}_p / R_u = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4,$$

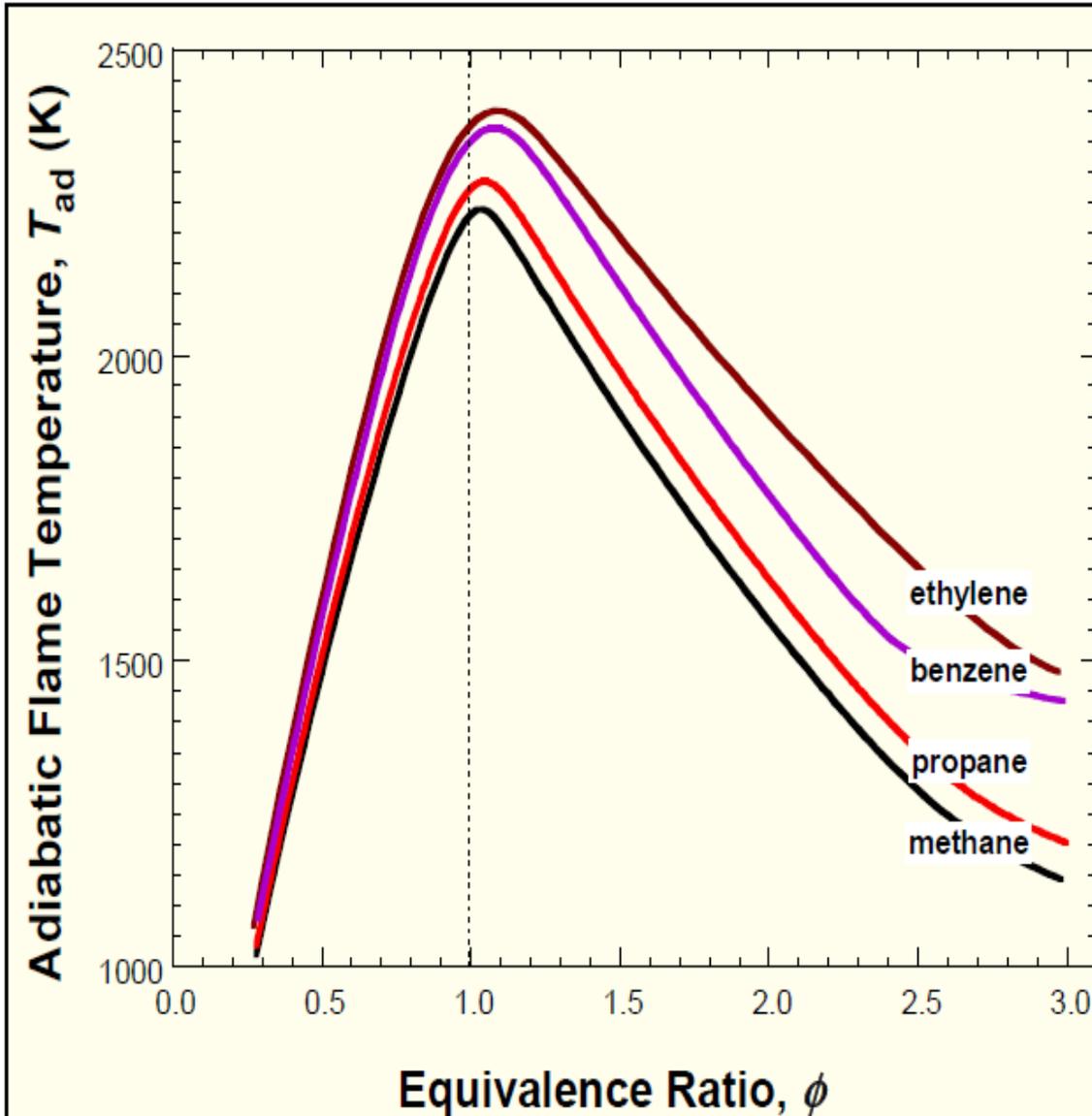
$$\bar{s}^0 / R_u = a_1 \ln T + a_2 T + a_3 T^2 / 2 + a_4 T^3 / 3 + a_5 T^4 / 4 + a_7.$$

$$\bar{h}_T / R_u = a_1 T + a_2 T^2 / 2 + a_3 T^3 / 3 + a_4 T^4 / 4 + a_5 T^5 / 5 + a_6$$

## LHV and UHV

- Fuels are classified by their Heating Value, i.e. their heat of combustion.
- Two variants are commonly used: Lower Heating Value and Upper Heating Value.
- LHV assumes all the  $H_2O$  formed is in gas phase, this is realistic for engines where the  $H_2O$  leaves in the exhaust. Note in a real engine the  $H_2O$  in the exhaust would be hot, but the LHV calculation usually assumes room temperature steam.
- UHV assumes all the  $H_2O$  formed is in liquid phase. This is realistic for bomb calorimetry experiments, where the final temperature is usually pretty low. So UHV is easier to measure. But it can be a big overestimate of the true heat delivered by the fuel in an engine.

# Adiabatic Flame Temperatures



Compute by noting  
 $H_{out}(T_{out}) = H_{in}(T_{in})$   
for an adiabatic process

Given  $H^o$ 's and  $C_p(T)$ 's  
and assuming stoichiometry,  
you can solve for  $T_{out}$

At true combustion  $T$ ,  
equilibrium concentrations of  
Species other than  $CO_2$  &  $H_2O$   
are significant...

Figure 1.2. Adiabatic flame  
temperature of methane,  
propane, ethylene and benzene  
at 1 atm pressure.

At low  $P$ , high  $T$ ,  $\text{CO}+\text{O}_2$  equilibrium important  
so Adiabatic Flame  $T$  varies a bit with  $P$

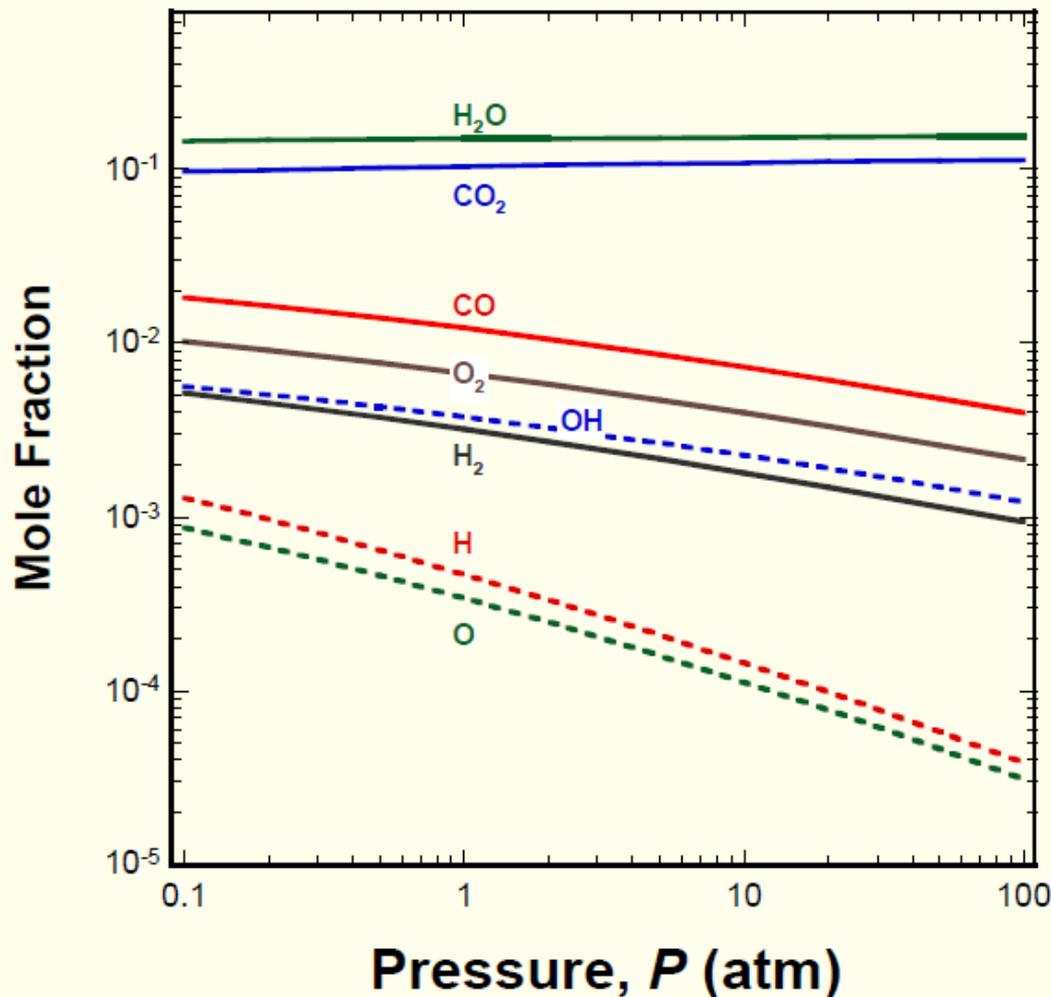


Figure 1.4. Mole fractions of equilibrium products computed for propane combustion in air at the unity equivalence ratio.

# Standard entropy

## Standard entropy

Based on the 3<sup>rd</sup> law of Thermodynamics:

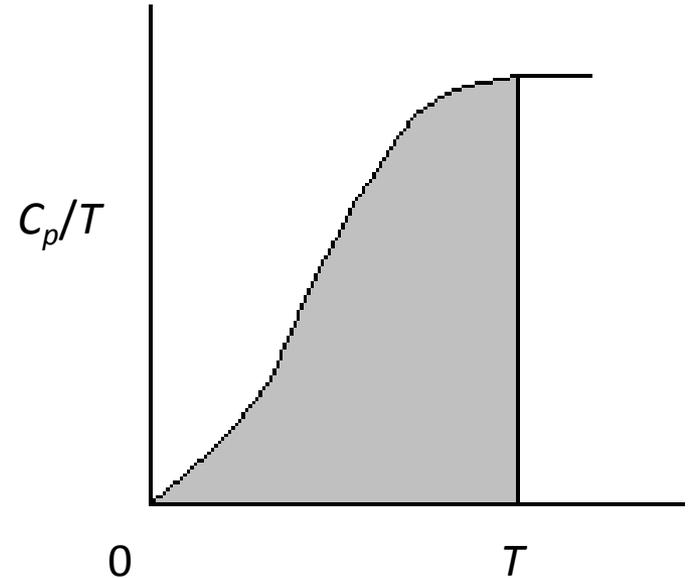
The entropy of any perfectly crystalline material at  $T = 0$  is zero

**Standard molar entropy,  $S_m^\ominus$**

The entropy of 1 mol of a substance in its standard state based on the 3<sup>rd</sup> law

Sometimes entropies of formation

are used, but this makes no difference to entropies of reaction provided consistency is maintained



NB – calculation using statistical mechanics – next slide

## Statistical Mechanics Basics

- There is a quantity  $Q$  called the "partition function"

$$Q = \sum g_i \exp(-E_i/k_B T)$$

where  $E_i$  are the possible energies of the molecule (quantum mechanics only allows certain quantized energies), and  $g_i$  is the number of quantum states with energy  $E_i$ .

- $Q$  contains enough information to compute all the normal thermochemical quantities. For example

$$\text{Helmholtz Free Energy} = U - TS = G - PV = -k_B T \ln Q$$

$$U(T,V) = k_B T^2 \partial(\ln Q)/\partial T$$

## Quantized Energies & Partition Functions

$$Q = \sum_i g_i \exp\left(\frac{-\epsilon_i}{kT}\right)$$

We usually approximate each of the vibrations in a molecule as a harmonic oscillator. (This is not always an accurate approximation, but it really simplifies the math!) The quantized energy of a harmonic oscillator with characteristic frequency  $\nu$  are:

$$E_{vib,n} = \left(n + \frac{1}{2}\right) h\nu \quad n = 0, 1, \dots ,$$

I recommend you choose the zero of energy to be the lowest state (all the vibrations have  $n_i=0$ ), and handle the zero-point-energy (ZPE) =  $\frac{1}{2} h \sum \nu_i$  separately. Then  $E_{vib} = h \sum n_i \nu_i$  and

$$q_{vib} = \prod (1 - \exp(-h\nu_i/k_B T))^{-1}$$

## Translational Partition Function (Particle in a Cube, $V=L^3$ )

$$E_{trans}(n_x, n_y, n_z) = \frac{b^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \dots$$

$$q_{trans}(V, T) = \sum_j e^{-\frac{b^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)/k_B T} \quad (2.46)$$

The summation cannot be performed in closed form but since the energy levels are closely spaced compared with  $k_B T$  it can be approximated by an integral

$$\begin{aligned} q_{trans}(V, T) &= \int_0^\infty \int_0^\infty \int_0^\infty e^{-\frac{b^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)/k_B T} dn_x dn_y dn_z \\ &= \left( \int_0^\infty e^{-\frac{b^2 n^2}{8mL^2}/k_B T} dn \right)^3, \\ &\approx \left( \frac{2\pi m k_B T}{b^2} \right)^{\frac{3}{2}} V \end{aligned} \quad (2.47)$$

## Rotational Partition Functions

For a Linear Molecule, assumed to be Rigid with Moment of Inertia "I":

$$E_{rot,J} = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, \dots,$$

Each J state has (2J+1) M states, so  $g = 2J+1$

Making a similar approximation as for translation, and considering the effects of symmetry (with symmetry number  $\sigma$ ), we obtain

$$q_{rot} \cong 8\pi^2 I k_B T / \sigma h^2$$

For nonlinear molecules there are 3 distinct moments of inertia  $I_a, I_b, I_c$

$$q_{rot\_nonlinear} \cong \pi^{\frac{1}{2}} q_{rot}^{3/2}$$

where  $I^{3/2}$  is replaced by  $\text{sqrt}(I_a * I_b * I_c)$

## Total partition function

Above we gave partition functions for certain motions of a single molecule in a volume  $V$ . For  $N$  identical non-interacting molecules in a volume  $V$  (e.g. an ideal gas):

$$Q = (q_{\text{vib}} q_{\text{trans}} q_{\text{rot}} q_{\text{elec}})^N / N!$$

$$\ln Q \sim N \ln (q_{\text{vib}} q_{\text{trans}} q_{\text{rot}} q_{\text{elec}}) - N \ln N$$

Conventionally people replace the  $V$  in  $q_{\text{trans}}$  with  $V/N = RT/P$  and just write

$$\ln Q = N \ln q$$

Where  $q = q_{\text{vib}} q_{\text{trans}} q_{\text{rot}} q_{\text{elec}}$  using the modified  $q_{\text{trans}}$

Note for most stable molecules there is only one accessible electronic state, so  $q_{\text{elec}} \sim 1$ . For most radicals  $q_{\text{elec}} \sim 2$ . For molecules with low-lying non-degenerate electronic states one should evaluate the partition function exactly.

If the molecules are interacting weakly (e.g. non-ideal gas), one can correct the expression above for  $Q$  using the Equation of State. For liquids  $q_{\text{rot}}$  and  $q_{\text{trans}}$  are significantly different, but usually  $q_{\text{vib}}$  stays about the same as in gas phase.

# Thermodynamic and spectroscopic data from NIST

- <http://webbook.nist.gov/chemistry/>
- E.g. Methane, gas phase. Selected thermodynamic data, ir spectra, vibrational and electronic energy levels

Quantity	Value	Units	Method	Reference
$\Delta_f H^\ominus$	-74.87	kJ mol <sup>-1</sup>	Review	Chase 1998
$\Delta_f H^\ominus$	-74.6±0.3	kJ mol <sup>-1</sup>	Review	Manion
$S^\ominus$	188.66±0.42	J mol <sup>-1</sup> K <sup>-1</sup>	N/A	Colwell 1963

Sym. Species	No	Approximate type of mode	Selected Freq. Value	Rating	Infrared Value	Phase	Raman Value	Phase	Comments
a <sub>1</sub>	1	Sym str	2917	A	ia		2917.0	gas	
e	2	Deg deform	1534	A	1533	ia gas	1533.6		Observed through Coriolis interaction with ν <sub>4</sub>
f <sub>2</sub>	3	Deg str	3019	A	3018.9	gas	3019.5		
f <sub>2</sub>	4	Deg deform	1306	C	1306.2	gas			

## Beware Internal Rotors & Floppy Motions!

- The normal vibrational partition function formulas are for harmonic oscillators.
- Some types of vibrational motions (torsions/internal rotations, umbrella vibrations, pseudorotations) are NOT harmonic.
  - E.g. rotations about C-C bonds
  - Puckering of 5-membered rings like cyclopentane
- Many of the entropy values in standard tables are derived using *approximate formulas* to account for internal rotation. Who knows what formulas they used to estimate other floppy motions. They can be significantly in error!
- If you care about the numbers, read the footnotes in the tables to see how the numbers were computed. Just because it is in a table does not mean it is Truth.
- Always read the error bars!!!

Often impossible to measure all the vibrational frequencies...  
so use quantum chemistry to fill in the gaps

- For many quantum chemistry methods, people have implemented software that efficiently computes the second derivatives of the potential energy surface

$$\partial^2 V / \partial x_m \partial y_n$$

- From the second derivatives, one can do normal-mode analysis to compute all the small-amplitude-limit vibrational frequencies  $\nu_i$
- It is hard (essentially impossible) to compute  $V$  exactly for multi-electron molecules. However, there are many good approximate methods: e.g. B3LYP, CCSD, CAS-PT2, MRCI, HF
  - After the slash is the name of the basis set used when expanding the molecular orbitals: e.g. 6-31G\*, TZ2P, etc.
- Currently, most people use Density Functional Theory approximations to compute the second derivatives of  $V$ , e.g. M08, M06, B3LYP, ...

# Computational Chemistry Comparison and Benchmark DataBase - <http://cccbdb.nist.gov/>

- The CCCBDB contains links to experimental and computational thermochemical data for a selected set of 1272 **gas-phase** atoms and molecules. Tools for comparing experimental and computational ideal-gas thermochemical properties
- **Species in the CCCBDB**
  - Mostly atoms with atomic number less than than 18 (Argon). A few have Se or Br.
  - Six or fewer heavy atoms and twenty or fewer total atoms. *Exception:* Versions 8 and higher have a few substituted benzenes with more than six heavy atoms. Versions 12 and higher have bromine-containing molecules.
- Specific experimental properties 1. Atomization energies 2. Vibrational frequencies 3. Bond lengths 4. Bond angles 5. Rotational constants 6. Experimental barriers to internal rotation

# Methane

HF/6-31G\*

Frequency in  $\text{cm}^{-1}$

	Calculated			Experimental		
Mode Number	Symmetry	Frequency	diff	Symmetry	Frequency	Comment
1	A <sub>1</sub>	<u>2872</u>	-45	A <sub>1</sub>	2917	
2	E	<u>1530</u>	-4	E	1534	
3	T <sub>2</sub>	<u>2966</u>	-53	T <sub>2</sub>	3019	
4	T <sub>2</sub>	<u>1337</u>	31	T <sub>2</sub>	1306	

The calculated vibrational frequencies were scaled by 0.8985

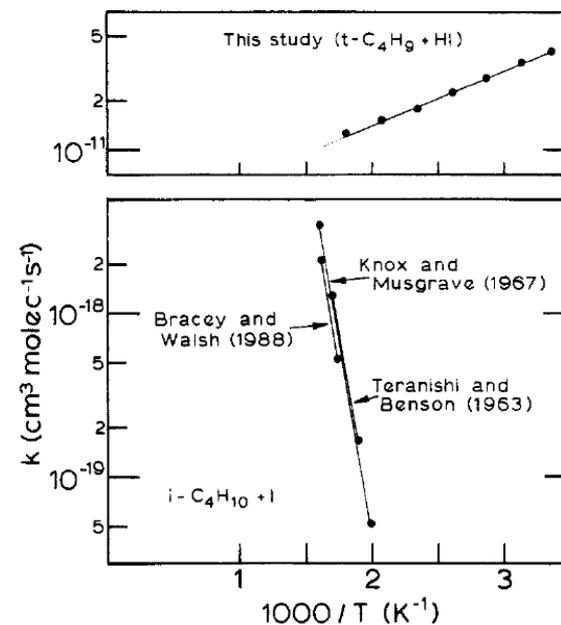
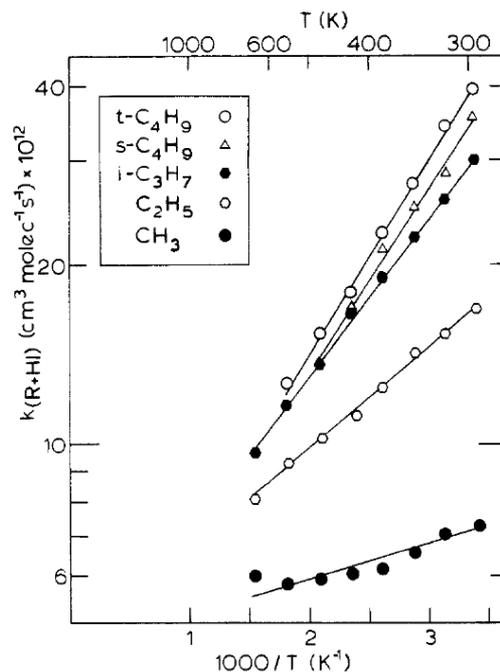
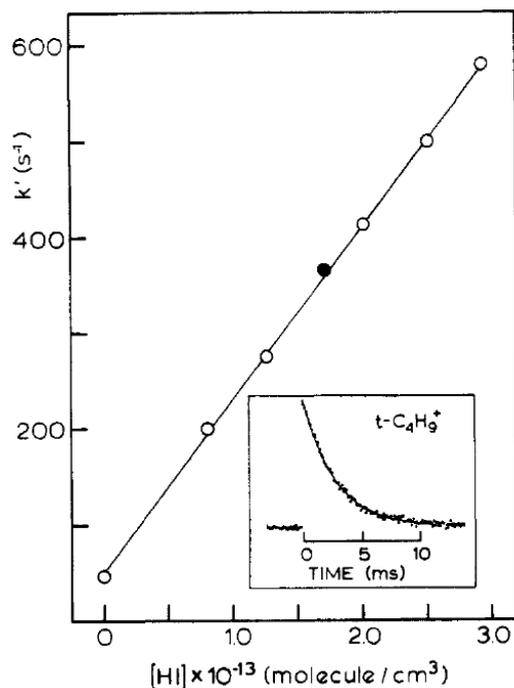
## Enthalpies of formation of radicals

- Enthalpies of formation of stable compounds, such as hydrocarbons, are determined from measurements of enthalpies of combustion, using Hess's Law.
- This approach is not feasible for radicals. An IUPAC evaluation of thermodynamic data for radicals can be found in Ruscic et al  
J Phys Chem Ref Data, 2005, 34, 573.
- Example:  $\text{CH}_3$ . Determined by:
  - Kinetics, e.g. J Am Chem Soc, 1990, 112, 1347
  - Photoionization spectroscopy, e.g. J Chem Phys, 1997, 107, 9852
  - Electronic structure calculations, e.g. J Chem Phys, 2001, 114, 6014
- Recommended value by IUPAC:  $\Delta_f H^\ominus(298.15 \text{ K}) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$

# Kinetics and thermodynamics of alkyl radicals

Seetula et al. *J Am Chem Soc*, 1990, 112, 1347

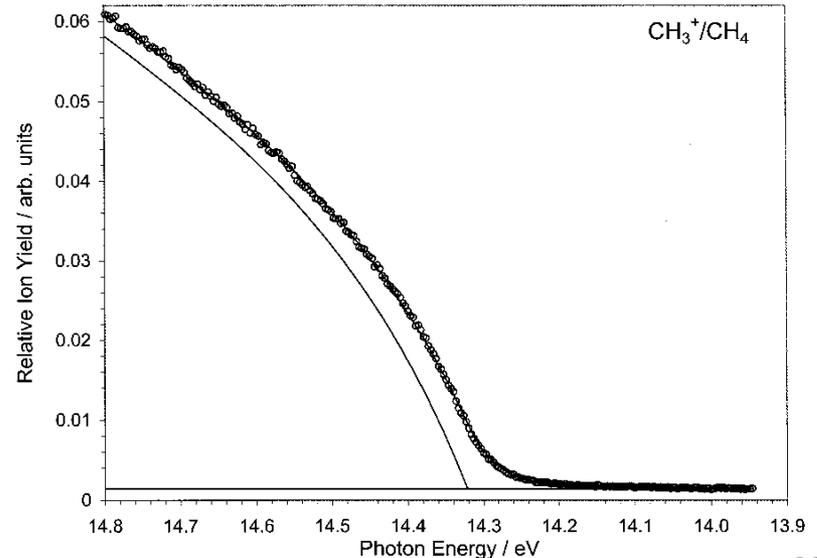
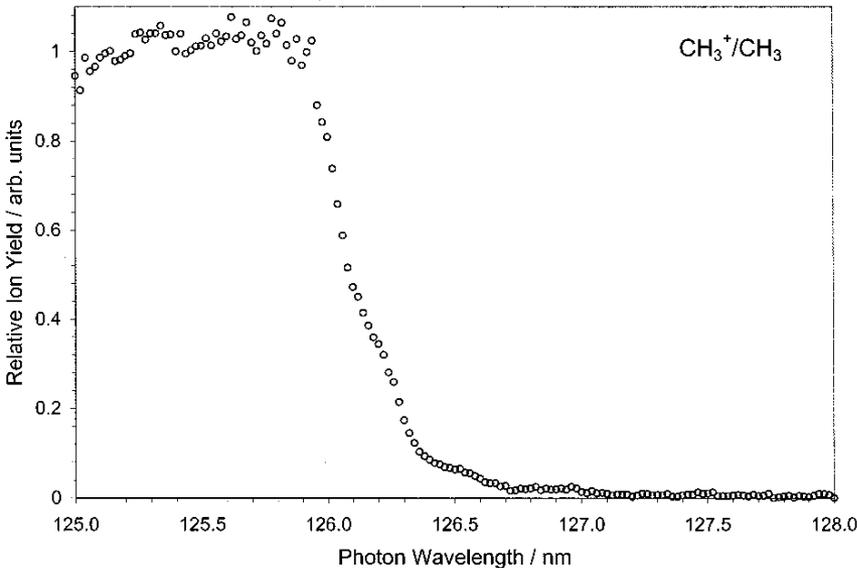
- Measured  $k(T)$  for  $R + HI$ , using laser flash photolysis / photoionization mass spectrometry, and combined with existing data for reverse reaction ( $I + RH$ ) to determine equilibrium constant. Enthalpy of reaction determined by second and third law methods



# Photoionization spectrum of $\text{CH}_3$

Litorja and Ruscic, J Chem Phys, 1997, 107, 9852

- Measure the photoionization threshold for  $\text{CH}_3$  and the appearance potential of  $\text{CH}_3^+$  from  $\text{CH}_4$  photexcitation. Obtain the dissociation energy of  $\text{CH}_3\text{-H}$ :



## Computed data (Quantum Chemistry)

- Geometries, vibrational frequencies, entropies, energies, means for comparing data



### B3LYP/6-311+G(3df,2p)

Frequency in  $\text{cm}^{-1}$

	Calculated			Experimental		
Mode Number	Symmetry	Frequency	diff	Symmetry	Frequency	Comment
1	$A_1'$	<u>3004</u>	-0	$A_1'$	3004	
2	$A_2''$	<u>523</u>	-84	$A_2''$	606	
3	$E'$	<u>3175</u>	14	$E'$	3161	
4	$E'$	<u>1361</u>	-35	$E'$	1396	

The calculated vibrational frequencies were scaled by 0.967

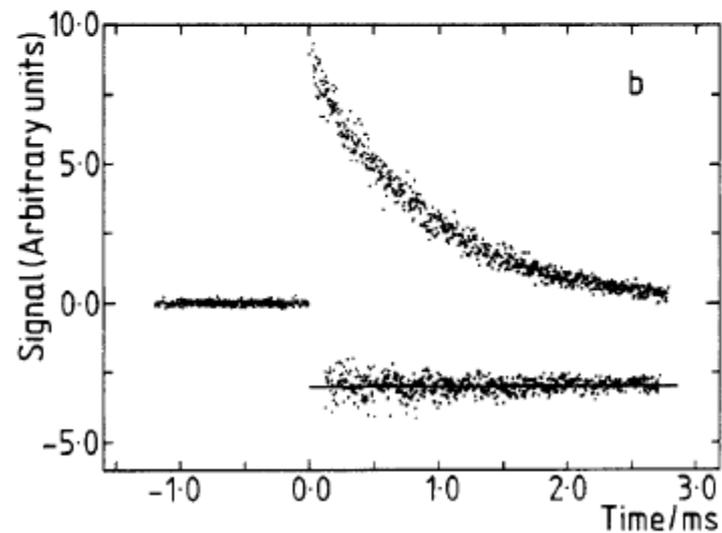
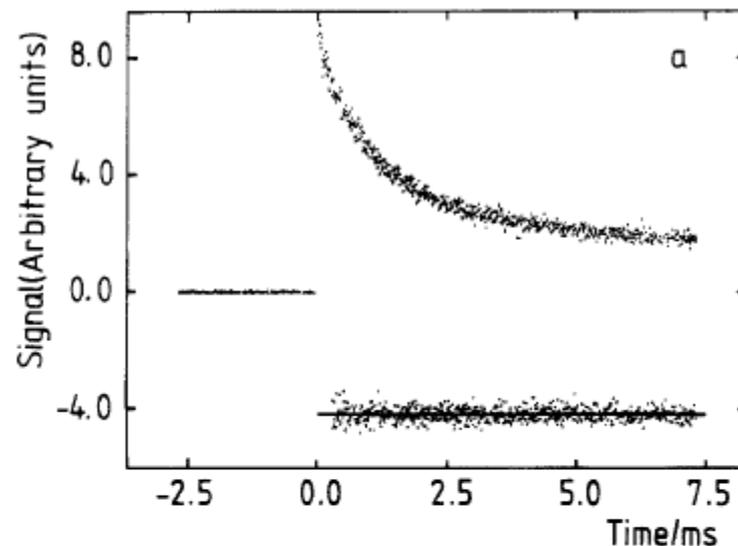
# Direct measurement of equilibrium constant for reactions involving radicals: $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$

- Brouard et al. J. Phys. Chem. 1986, 90,445-450
- Laser flash photolysis, H atom resonance fluorescence.

• Reactions involved:



- Solve rate equations - gives bi-exponential decay of H,  $k_1$  and  $k_{-1}$  and hence  $K_1$  from analysis. Vary T, enthalpy of reactions from second or third law.



## R-H bond energies: Extensive tabulation and review Berkowitz et al. 1994, 98, 2744

- The bond enthalpy change at 298 K is the enthalpy change for the reaction  $R-H \rightarrow R + H$ :

$$DH_{298}(R-H) = \Delta_f H_{298}(R) + \Delta_f H_{298}(H) - \Delta_f H_{298}(RH)$$

- The bond energy (change) or dissociation energy at zero K is:

$$D_0(R-H) = E_0(R) + E_0(H) - E_0(RH)$$

- Bond energies can be converted to bond enthalpy changes using the relation  $U = H + pV = H + RT$ , so that, for  $R-H \rightarrow R + H$ ,  $\Delta U = \Delta H + RT$ . At zero K, the dissociation energy is equal to the bond enthalpy change.
- Berkowitz et al provide an extensive dataset for R-H bond energies using radical kinetics, gas-phase acidity cycles, and photoionization mass spectrometry

# Thermodynamic databases

- Active, internally consistent thermodynamic databases:
  - ATcT Active thermochemical tables. Uses and network approach. Ruscic et al. J. Phys. Chem. A 2004, 108, 9979-9997.
  - NEAT . Network of atom based thermochemistry. Csaszar and Furtenbacher: Chemistry - A european journal, 2010,16, 4826

# A Grid Service-Based Active Thermochemical Table Framework von Laszewski et al.

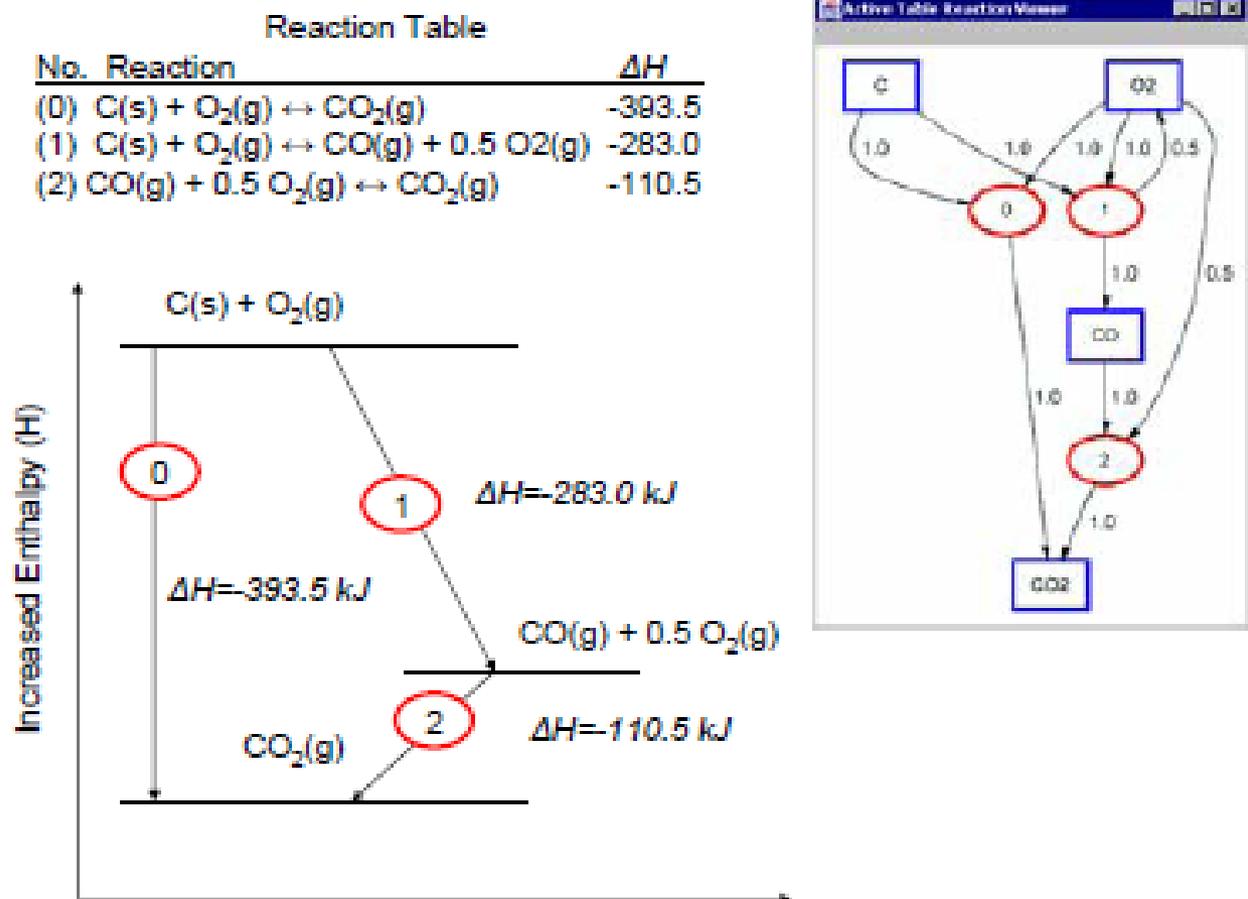


Fig. 1. Enthalpy diagrams and thermochemical reaction tables.

An  
Part of a  
thermo-  
chemical  
network  
showing  
the basic  
ideas

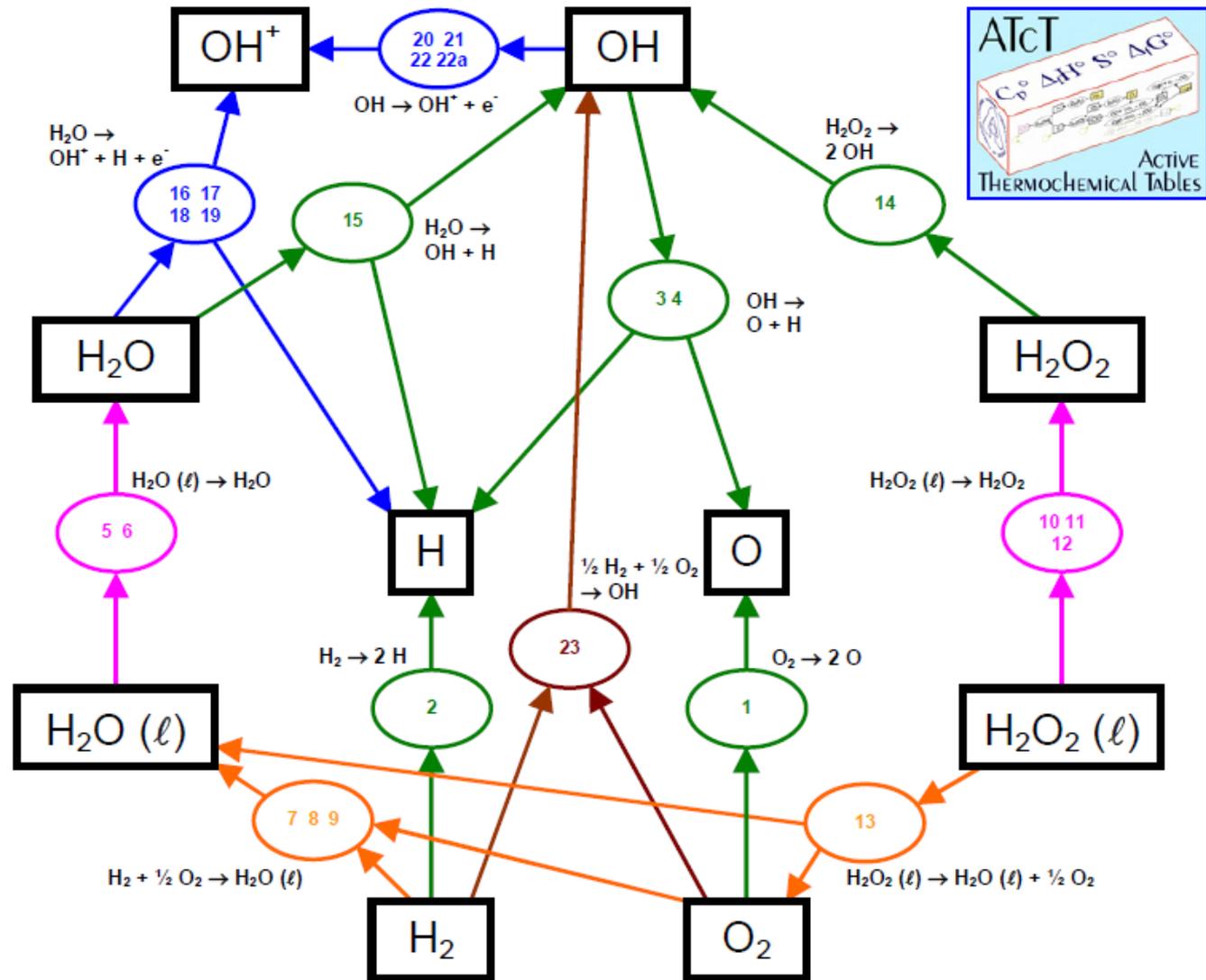
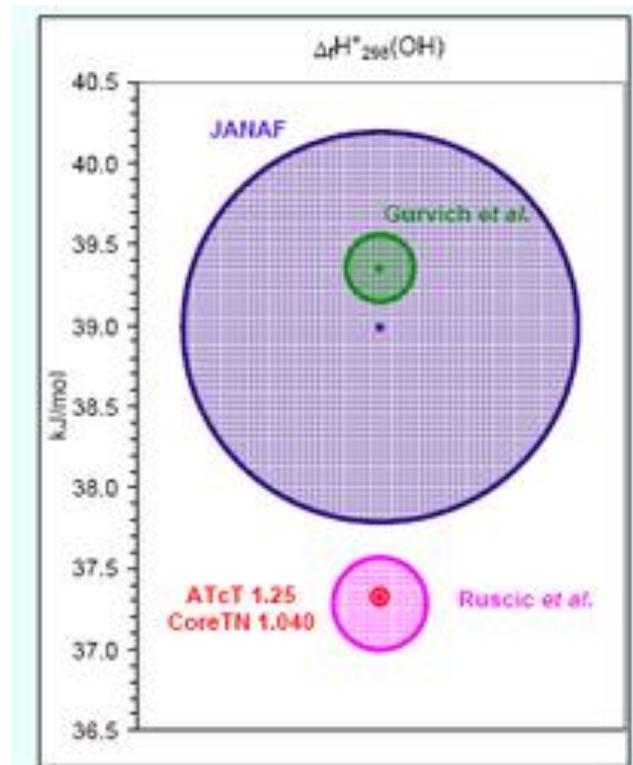


Figure 1. A small subsection of the current Core (Argonne) Thermochemical Network. The full network currently contains >600 primary vertices and >3200 secondary vertices. See text for further details



# Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical

Ruscic et al. J Phys Chem, 2001, 105, 1

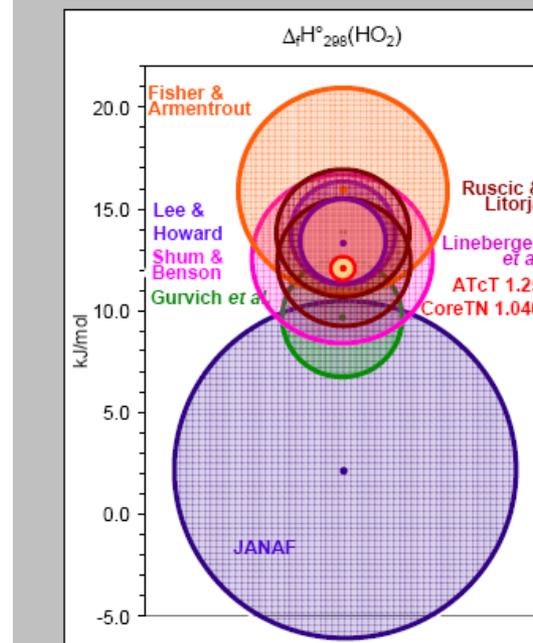


**TABLE 1: Various Values for the 0 K Enthalpy of Formation of OH and Related Values for  $D_0(\text{H}-\text{OH})$  and  $D_0(\text{OH})^a$**

source	$\Delta H_{f0}(\text{OH})$	$D_0(\text{H}-\text{OH})$	$D_0(\text{OH})$
Gurvich et al., <sup>b</sup> following Carlone and Dalby <sup>c</sup>	$9.35 \pm 0.05$ kcal/mol	$118.08 \pm 0.05$ kcal/mol <sup>d</sup> ( $41301 \pm 17$ cm <sup>-1</sup> )	$101.27 \pm 0.04$ kcal/mol ( $35420 \pm 15$ cm <sup>-1</sup> )
Barrow <sup>e</sup>	$9.26 \pm 0.29$ kcal/mol	$118.00 \pm 0.29$ kcal/mol <sup>d</sup> ( $41270 \pm 100$ cm <sup>-1</sup> )	$101.36 \pm 0.29$ kcal/mol ( $35450 \pm 100$ cm <sup>-1</sup> )
JANAF <sup>f</sup>	$9.18 \pm 0.29$ kcal/mol	$117.91 \pm 0.29$ kcal/mol <sup>d</sup> ( $41240 \pm 100$ cm <sup>-1</sup> )	$101.44 \pm 0.29$ kcal/mol ( $35480 \pm 100$ cm <sup>-1</sup> )
recommended values, present experiment <sup>g</sup>	$8.83 \pm 0.09$ kcal/mol	$117.57 \pm 0.09$ kcal/mol ( $41120 \pm 30$ cm <sup>-1</sup> )	$101.79 \pm 0.09$ kcal/mol <sup>h</sup> ( $35600 \pm 30$ cm <sup>-1</sup> )
present calculation	$8.87 \pm 0.16$ kcal/mol	$117.61 \pm 0.16$ kcal/mol <sup>d</sup> ( $41135 \pm 55$ cm <sup>-1</sup> )	$101.74 \pm 0.16$ kcal/mol ( $35585 \pm 55$ cm <sup>-1</sup> )

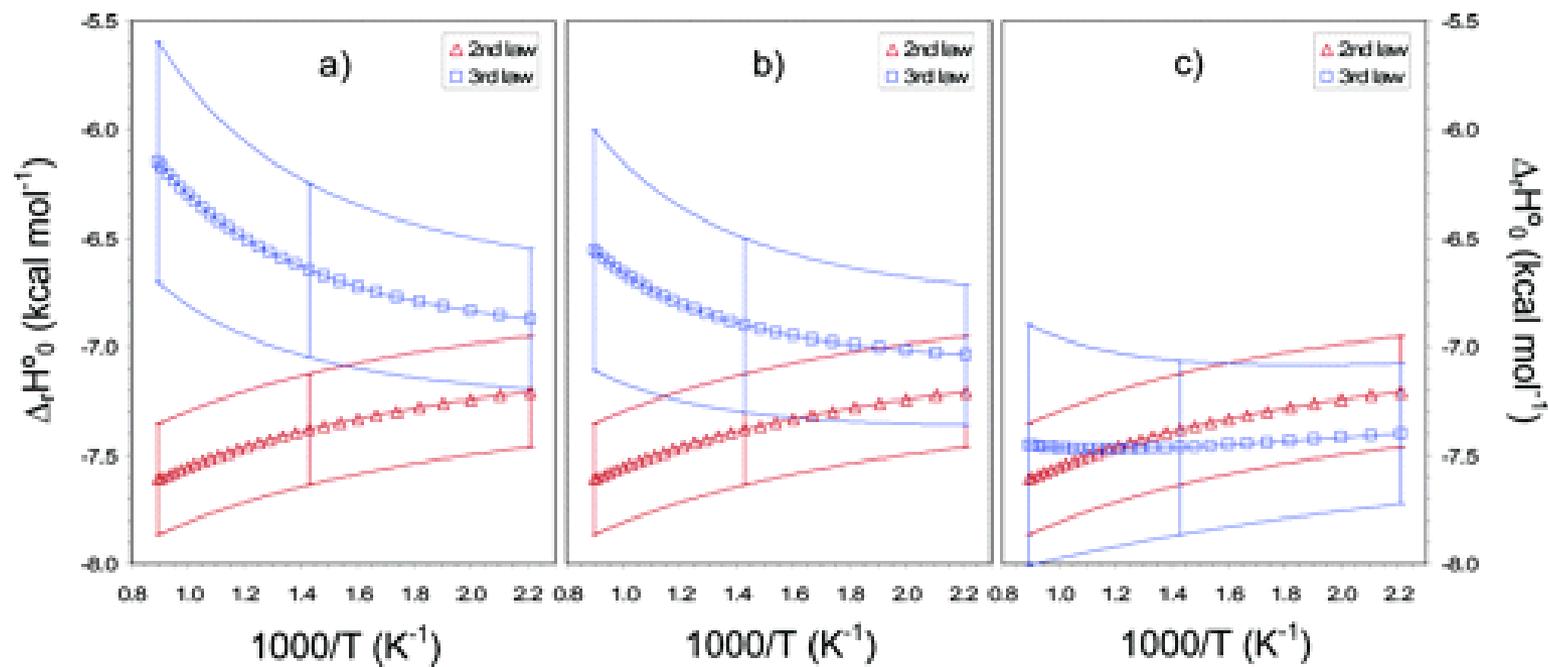
# Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO<sub>2</sub>

Ruscic et al., *J. Phys. Chem. A*  
2006, 110, 6592-6601



“Howard reaction”  
OH + NO<sub>2</sub> → HO<sub>2</sub> + NO

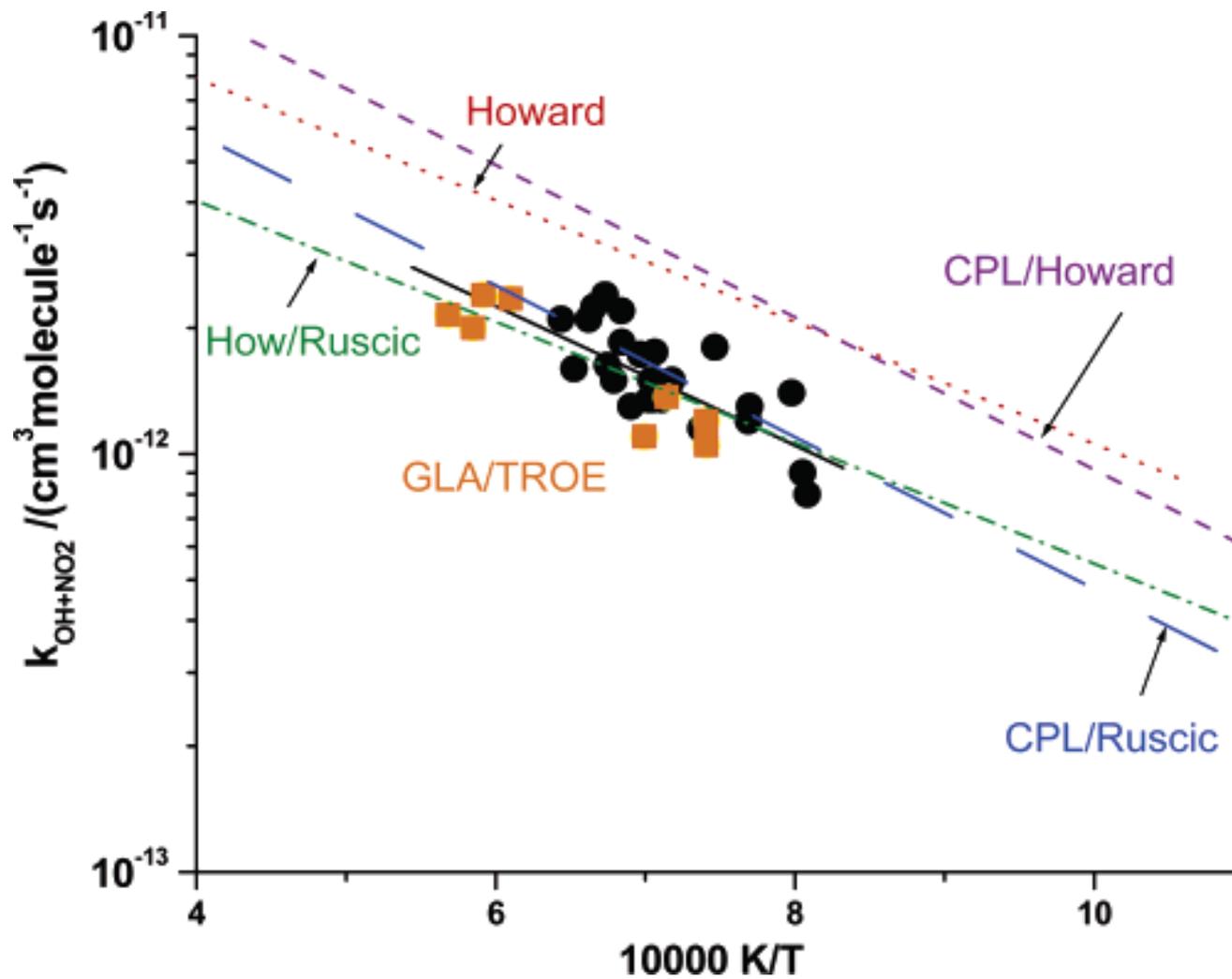
ATcT thermo + new kinetic experiments (J. Michael, ANL):  
the reverse rate was indeed off by a factor of 2!



**TABLE 1: Available Experimental Values for the Standard Enthalpy of Formation of HO<sub>2</sub> at 298 K (in kcal mol<sup>-1</sup>)<sup>a</sup>**

source	originally reported value <sup>b</sup>	revised value <sup>c</sup>
JANAF Tables <sup>10,11</sup>	0.5 ± 2.0	
Gurvich et al. <sup>19</sup>	2.3 ± 0.7	
Howard <sup>20</sup>	2.5 ± 0.6	2.0 ± 0.6
Lee and Howard <sup>21</sup>	3.3 ± 0.6	3.2 ± 0.6
Hills and Howard <sup>23</sup>	3.0 ± 0.4	2.9 ± 0.4
Shum and Benson <sup>24,25</sup>	> 3.0	
Heneghan and Benson <sup>26</sup>	4.6 ± 0.2	
Heneghan and Benson <sup>29</sup>	> 3.4	
Fisher and Armentrout <sup>30</sup>	3.8 ± 1.2	3.2 ± 1.2
Litorja and Ruscic <sup>31</sup>	3.3 ± 0.8	2.9 ± 0.6 <sup>d</sup>
Clifford et al. <sup>32</sup>	3 ± 1	
Ramond et al. <sup>35</sup>	3.2 ± 0.5	3.2 ± 0.5
ATcT, current work <sup>e</sup>	2.94 ± 0.06	

## Comparison with Howard data



## Example of current accuracy in ATcT



B. Ruscic, private communication of unpublished ATcT datum from ver. 1.112 of ATcT TN (2012)

- the enthalpy of the reaction is equivalent to the difference in bond dissociation energies of  $\text{H}_2$  and  $\text{CH}_2$ , and noting that  $D_0(\text{CH}_2) = \text{TAE0}(\text{CH}_2) - \text{TAE0}(\text{CH})$ , the recently published ATcT total atomization energies (TAE0) for  $\text{CH}_2$  and  $\text{CH}$  and the ATcT enthalpy of formation for  $\text{H}$  produce a quite accurate 0 K enthalpy of the reaction of  $3.36 \pm 0.08$  kcal/mol ( $14.04 \pm 0.35$  kJ/mol). The latest ATcT value is nearly identical,  $3.38 \pm 0.04$  kcal/mol ( $14.15 \pm 0.18$  kJ/mol), though it has further gained in accuracy due to additional refinements of the ATcT TN
- Propagating the uncertainty in the equilibrium constant:

$$\ln K = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$
$$\sigma_{\ln K}^2 = \frac{\sigma_{\Delta_r H^\ominus}^2}{(RT)^2} + \frac{\sigma_{\Delta_r S^\ominus}^2}{R^2}$$

- Determine  $\sigma_{\ln K}^2$  at 1000 K for combustion applications and at 10 K for applications in interstellar chemistry.

# From a Network of Computed Reaction Enthalpies to Atom-Based Thermochemistry (NEAT)

A. G. Csaszar and T. Furtenbacher,

Chemistry - A european journal, 2010,16, 4826

Abstract: A simple and fast, weighted, linear least-squares refinement protocol and code is presented for inverting the information contained in a network of quantum chemically computed 0 K reaction enthalpies. This inversion yields internally consistent 0 K enthalpies of formation for the species of the network.

# NEAT - protocol

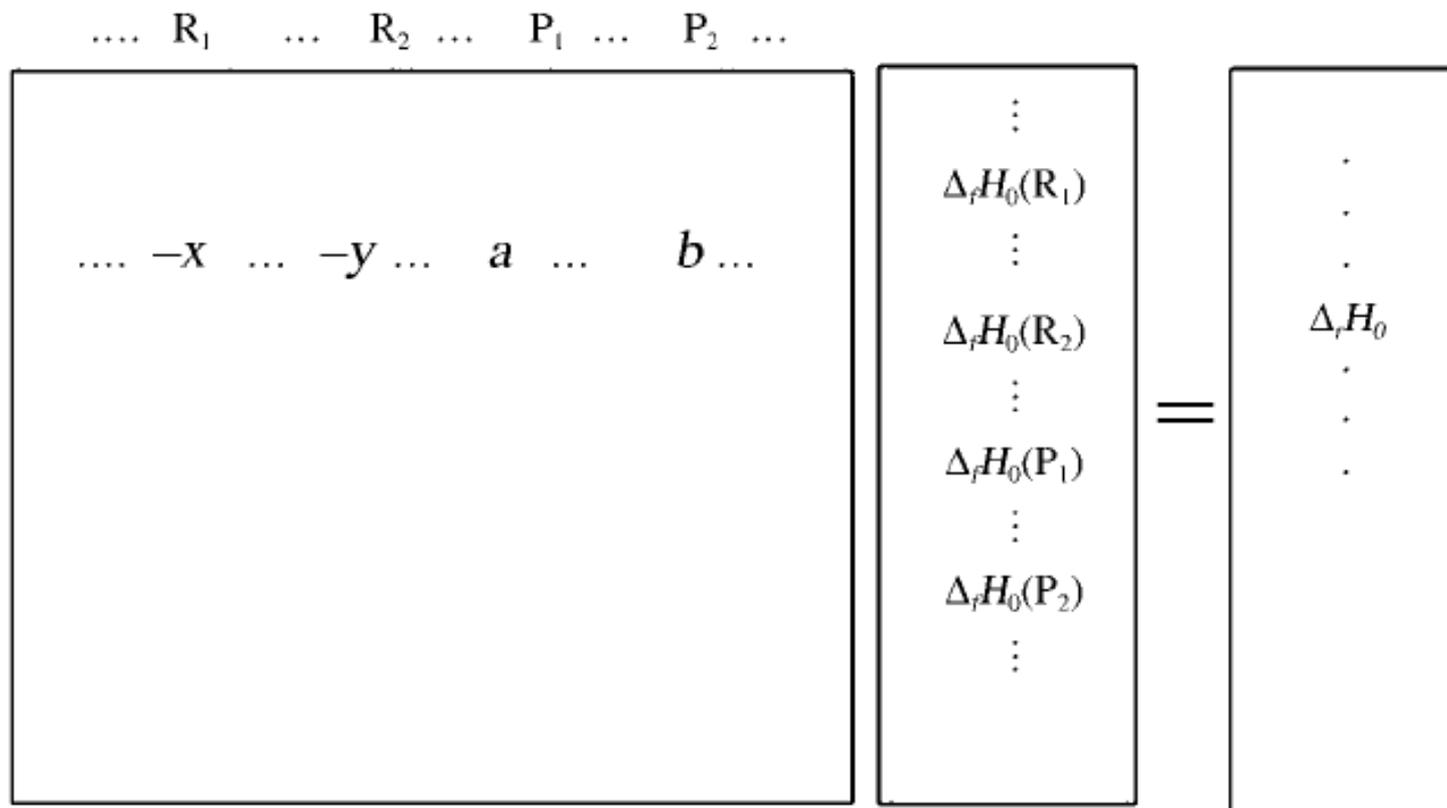


Figure 1. Pictorial representation of the NEAT protocol, which, after an inversion, leads to 0 K enthalpies of formation ( $\Delta_f H_0$ ) from computed reaction enthalpies ( $\Delta_r H_0$ ).

## Incorporation of thermodynamics data into rate calculations:

Burcat: <http://garfield.chem.elte.hu/Burcat/burcat.html>

- Provides data in NASA polynomial form, with 7 parameters that are related to necessary thermodynamic functions of state via:

$$C_p/R = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$H/RT = a_1 + a_2 T / 2 + a_3 T^2 / 3 + a_4 T^3 / 4 + a_5 T^4 / 5 + a_6/T$$

$$S/R = a_1 \ln T + a_2 T + a_3 T^2 / 2 + a_4 T^3 / 3 + a_5 T^4 / 4 + a_7$$

Where  $H(T) = \Delta H_f(298) + [ H(T) - H(298) ]$

- Linked to ATcT and used in Chemkin.

## Burcat database. Entry for CH<sub>3</sub>

- CH3 METHYL-RAD STATWT=1. SIGMA=6.  
IA=IB=.2923 IC=.5846 NU=3004,606.4,3161(2),  
1396(2) HF298=146.7 +/-0.3 KJ HF0=150.0+/-0.3 kJ  
REF= Ruscic et al JPCRD 2003. {HF298=146.5+/-0.08  
kJ REF=ATcT C} Max Lst Sq Error Cp @ 6000 K  
0.44%. METHYL RADICAL IU0702C 1.H 3. 0. 0.G  
200.000 6000.000 B 15.03452 1
- 0.29781206E+01 0.57978520E-02 -0.19755800E-05  
0.30729790E-09 -0.17917416E-13 2
- 0.16509513E+05 0.47224799E+01 0.36571797E+01  
0.21265979E-02 0.54583883E-05 3
- -0.66181003E-08 0.24657074E-11 0.16422716E+05  
0.16735354E+01 0.17643935E+05 4
- First 7 entries are a1-7 for 1000 - 6000 K. 2<sup>nd</sup> set are  
a1-a7 for 200 - 1000 K. Temp ranges specified in line  
1

Table 1.2 Standard enthalpy of formation of key combustion species in the vapor state

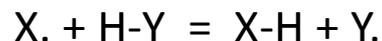
Species	Name	$\bar{h}_{f,298}^{\circ}$ (kJ/mol)
H <sub>2</sub> O	Water	-241.8
CO	Carbon monoxide	-110.5
CO <sub>2</sub>	Carbon dioxide	-393.5
CH <sub>4</sub>	Methane	-74.9
C <sub>2</sub> H <sub>6</sub>	Ethane	-84.8
C <sub>3</sub> H <sub>8</sub>	Propane	-104.7
C <sub>4</sub> H <sub>10</sub>	Butane	-125.6
C <sub>8</sub> H <sub>18</sub>	Octane	-208.4
C <sub>2</sub> H <sub>4</sub>	Ethylene	52.5
C <sub>2</sub> H <sub>2</sub>	Acetylene	226.7
CH <sub>3</sub> OH	Methanol	-201.0
C <sub>6</sub> H <sub>6</sub>	Benzene	82.9
H•	Hydrogen atom	218.0
O•	Oxygen atom	248.2
OH•	Hydroxyl radical	39.0

## Very helpful to know typical bond energies

Table 2.2 Typical C-C and C-H bond energies ( $D_{e,298K}$ , kJ/mol).

atom or group	methyl CH <sub>3</sub>	ethyl C <sub>2</sub> H <sub>5</sub>	<i>i</i> -propyl (CH <sub>3</sub> ) <sub>2</sub> CH	<i>t</i> -butyl (CH <sub>3</sub> ) <sub>3</sub> C	phenyl C <sub>6</sub> H <sub>5</sub>	benzyl C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	allyl C <sub>3</sub> H <sub>5</sub>	acetyl CH <sub>3</sub> CO	vinyl C <sub>2</sub> H <sub>3</sub>	ethynyl C <sub>2</sub> H
H	439	420	413	400	474	375	369	377	465	547
OH	384	392	400	398	473	339	332		464	552
CH <sub>3</sub>	375	369	370	362	435	323	317	352	424	516
C <sub>2</sub> H <sub>5</sub>	369	364	363	353	428	318		346	419	510
(CH <sub>3</sub> ) <sub>2</sub> CH	370	363	358	343	425	319		341		510
(CH <sub>3</sub> ) <sub>3</sub> C	362	353	343	322	410			327		498
C <sub>6</sub> H <sub>5</sub>	435	428	425	410	496	381		414	491	588
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	323	318	319		381	278		290		

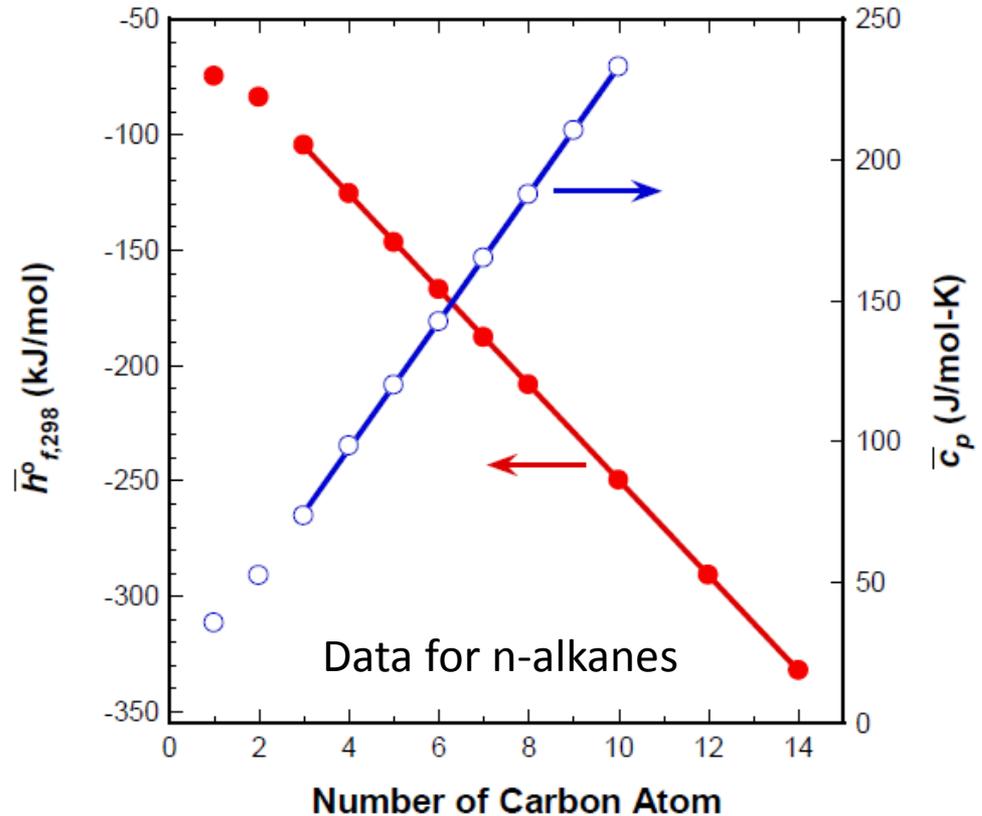
Many of the most important reactions in combustion are H-abstractions of the form



The barrier is lower in the exothermic direction,  $E_{a,reverse} \sim E_{a,forward} - \Delta H_{rxn}$  and often the weakest X-H bond is the one that reacts the fastest.

# Group Additivity

- Experimentally, for alkanes it is observed that  $H$ ,  $S$ , and  $C_p$  all vary linearly with the number of Carbons
- One can assign a value to the increments caused by inserting one more  $CH_2$  group into the alkane chain.
- This approach works for many different chemical functional groups: adding the group to the molecule adds a set amount to  $H$ ,  $S$ ,  $C_p$  called a *GAV*.
- For  $S$ , need to add a symmetry correction to the sum of the *GAV*.



S.W. Benson constructed tables of these Group Additivity Values (GAV). Several researchers, especially Bozzelli and Green, have added to these tables using quantum chemistry to fill in gaps in experimental data.

## Programs to estimate thermo with Group Additivity

- <http://webbook.nist.gov/chemistry/grp-add/>
- THERGAS (Nancy group)
- THERM (Bozzelli)
- RMG (Green group, MIT)
- Several others...

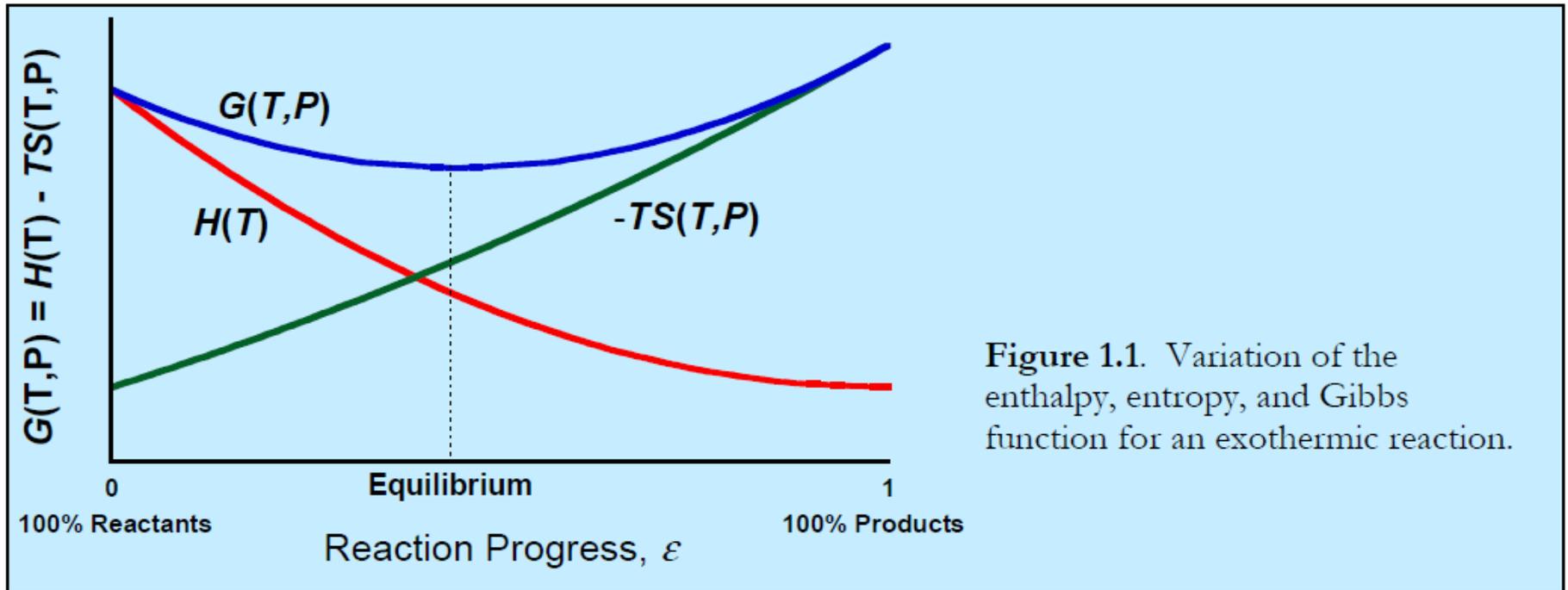
All of these programs are based on Benson's methods described in his textbook "Thermochemical Kinetics" and in several papers by Benson. See also several improvements to Benson's method by Bozzelli.

Group additivity is related to the "functional group" concept of organic chemistry, and to "Linear Free Energy Relationships" (LFER) and "Linear Structure-Activity Relationships" (LSAR).

## Problems with Group Additivity

- While the group additivity method is intuitively simple, it has its drawbacks stemming from the need to consider higher-order correction terms for a large number of molecules. Take cyclopentane as an example, the addition of group contributions yields  $H^{\circ} = -103$  kJ/mol, yet the experimental value is  $-76$  kJ/mol. The difference is caused by the ring strain, which is not accounted for in the group value of C-(C<sub>2</sub>H<sub>2</sub>) obtained from unstrained, straight-chain alkane molecules.
- Cyclics are the biggest problem for group additivity, but some other species also do not work well, e.g. some halogenated compounds, and some highly branched compounds. Very small molecules are often unique (e.g. CO, OH), so group additivity does not help with those.
- Species with different resonance forms can also cause problems, e.g. propargyl CH<sub>2</sub>CCH can be written with a triple bond or two double bonds, which should be used when determining the groups?

# Equilibrium minimizes Free Energy $G$



Free Energy Minimizer Software is Available.  
See e.g. EQUIL in CHEMKIN package.

# Computational Kinetics, Part 1

## Rate Theory

## Review Articles

### **The Current Status of Transition State Theory**

Donald G. Truhlar, Bruce C. Garrett, and Stephen J. Klippenstein  
J. Phys. Chem. (Centennial Issue) **100**, 12771-12800 (1996).

### **RRKM Theory and Its Implementation**

Stephen J. Klippenstein, in Comprehensive Chemical Kinetics, **39**, 55, (2003).

### **Modeling the Kinetics of Bimolecular Reactions**

Antonio Fernandez Ramos, James A. Miller, Stephen J. Klippenstein, and Donald G. Truhlar, Chem. Rev., **106**, 4518-4584 (2006).

### **Predictive Theory for Hydrogen Atom-Hydrocarbon Radical Association Kinetics**

Lawrence B. Harding, Yuri Georgievskii, and Stephen J. Klippenstein  
J. Phys. Chem. A, feature article, **109**, 4646-4656 (2005).

### **Predictive Theory for the Association Kinetics of Two Alkyl Radicals**

Stephen J. Klippenstein, Yuri Georgievskii, and Lawrence B. Harding  
Phys. Chem. Chem. Phys., invited article, **8**, 1133-1147 (2006).

### **Master Equation Methods in Gas Phase Chemical Kinetics**

James A. Miller and Stephen J. Klippenstein  
J. Phys. Chem. A, feature article, **110**, 10528-10544 (2006).

### **Ab Initio Methods for Reactive Potential Surfaces**

Lawrence B. Harding, Stephen J. Klippenstein, and Ahren W. Jasper  
Phys. Chem. Chem. Phys., **9**, 4055-4070 (2007).

# Start with Born-Oppenheimer approximation

- Electrons are light and have high kinetic energies, so they move very fast compared to the nuclei. So expect nuclei to feel time-averaged force exerted by swarm of electrons.
- Electrons are very quantum mechanical (wave-like, Pauli-exclusion principle). Described by Schroedinger's Wave Equation.
- Atoms/Nuclei are much heavier, move slowly, act like classical particles (mostly). Treat them with classical mechanics with some corrections.
- So solve the electron-motion problem first, assuming the nuclei are stationary at different geometries  $R$ , yielding a potential field  $V(R)$  that the nuclei are moving in.
  - Done with programs such as GAUSSIAN or MOLPRO
  - Hard problem, so we use basis set expansions & approximations like CCSD(T) or DFT
- How can we use computed  $V(R)$  to compute rate coefficients  $k(T)$ ?

# How does one compute a rate coefficient using classical mechanics?

First, assume *ergodicity*, i.e. all phase space  $(q,p)$  is equally likely to be sampled, biased only by Boltzmann weighting and conservation laws.

Divide phase space into “reactant” and “product” regions by specifying dividing surface  $s^\pm(q)=0$ .

Sample from “reactant” phase space, and see how fast each trajectory moves from reactant to product. (Only count trajectories which spend significant time as “products”; if they immediately bounce back to reactants we ignore them.) The average time it takes to move from reactant to product is related to the rate coefficient.

$$k = \int d\mathbf{q}d\mathbf{p}P(\mathbf{q},\mathbf{p})\delta(s - s^\ddagger)\chi(\mathbf{q},\mathbf{p})\frac{p_s}{m}$$

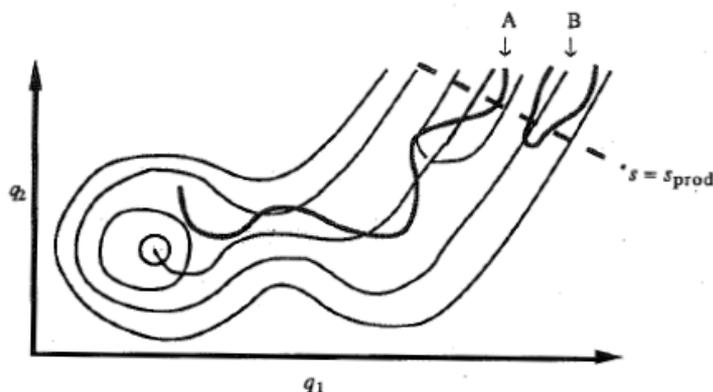


Fig. 2.14. The rate coefficient can be found from velocity with which a trajectory (denoted A) that started in the reactant valley crosses the line  $s = s_{\text{prod}}$  in the product valley. Trajectories which do not go into the reactant valley, such as that denoted B, must not be counted.

$s = s^\ddagger$  defines dividing surface

$p_s/m$  = velocity through  $s^\ddagger$

$\chi$  = reactivity function

- 1 if trajectory is reactive

- 0 otherwise

Trajectory Expression  
for the Rate Constant

$P(\mathbf{q},\mathbf{p})$

probability of specific  $\mathbf{q},\mathbf{p}$

Statistical  
Assumption

Canonical

$$P(\mathbf{q},\mathbf{p}) = \frac{\exp[-\beta H(\mathbf{q},\mathbf{p})]}{\int d\mathbf{q}d\mathbf{p}\exp(-\beta H)}$$

Microcanonical

$$P(\mathbf{q},\mathbf{p}) = \frac{\delta(E - H)}{\int d\mathbf{q}d\mathbf{p}\delta(E - H)}$$

Microcanonical J-Resolved

$$P(\mathbf{q},\mathbf{p}) = \frac{\delta(E - H)\delta(J - J_T)}{\int d\mathbf{q}d\mathbf{p}\delta(E - H)\delta(J - J_T)}$$

Theory of Unimolecular and Recombination Reactions; R. G. Gilbert and S. C. Smith, Blackwell Scientific

With the Transition State Assumption of No Recrossing, and choosing  $s^\pm = q^\pm$ , a special coordinate with value of zero at dividing surface, the Classical Phase Space Integrals can be rewritten this pretty way:

$$k(T) = \frac{k_B T}{h} \frac{Q^\pm}{Q_{\text{reac}}} \exp(-E^\pm / k_B T)$$

Where  $E^\pm = \text{lowest } V(R) \text{ with } q^\pm=0 \text{ (i.e. on the dividing surface)}$   
 minus lowest  $V(R)$  in reactant space.

$$Q_{\text{reac}} = \int dp dq \exp(-\beta H) (1-\Theta(q^\pm))/h^{3N}$$

i.e. it is the integral over the “reactant” phase space, and

$$Q^\pm = \int dp dq \exp(-\beta H(q^\pm = 0, p^\pm = 0)) / h^{3N-1}$$

with no integration over  $q^\pm$  or  $p^\pm$ . This integral is on dividing surface.

# Transition State Assumption and the Variational Principle

## Transition State Assumption

- Assume all trajectories with positive velocity through dividing surface are reactive
- Replace  $\chi$  with  $\Theta(p_s/m)$

In Reality  $\Theta(p_s/m) \geq \chi$

- $k_{\text{TST}} \geq k_{\text{Trajectory}}$

$\Rightarrow$  Variational Principle

$\Theta$  is the Heaviside function:  
 $\Theta(x) = 1$  if  $x > 0$ , zero otherwise.

## Variational Transition State Theory

- Consider family of TS dividing surfaces
- Best Dividing Surface is one that provides minimum estimate for  $k$

# Why use Transition State Theory?

Chemical Models Need Rate Coefficients for 1000's of Reactions

## Experiments

- Too time consuming
- Often can't perform experiments at T,P of interest

## Theory

- Empirical Models
  - Correlations and extensions of related experiments
  - Greater accuracy desirable
- Classical Trajectories
  - Need global potential energy surface
  - No quantum effects
  - Timescale  $\sim 1$  ns or shorter
- Quantum Dynamics
  - Too computationally intensive
  - 4 Atom Systems
- Transition State Theory
  - Compromise of Efficiency and Accuracy

However, we cannot completely ignore quantum mechanics for atomic motions...

- There is an exact quantum mechanical operator corresponding to the classical phase space integrals, with and without the transition state assumption, see W.H. Miller papers.
  - Exact version is expensive, biggest case done so far is  $\text{CH}_4 + \text{H}$ , by Manthe.
  - Several different approximations to the exact formula have been proposed, no consensus yet on best way to proceed.
- Some people just ignore the quantum mechanics, and do classical calculations, either phase space integrals or molecular dynamics. But neglecting zero-point-energy of vibrations is a big approximation, and there are also issues about rare-event sampling.
- Several patches to molecular dynamics try to include zero point energy approximately. You may be interested in the RPMD method (see RPMDRate program) which avoids some of the TS approximations.
- **If you are willing to make the TS approximations and some other approximations, you get a cheap and convenient recipe for computing rates...**

# Conventional TST Recipe

- Conventional (approximate) TST recipe:
  - Replace the Q's with the conventional RRHO formulas used for thermo
  - Use  $q_{\text{trans}}/(V/N)$  rather than dimensionless  $q_{\text{trans}}$  proportional to V
  - Correct  $E^\ddagger$  with zero-point-energy difference between reactant and TS.
  - If mirror-image TS's: factor of 2 in symmetry numbers
  - Multiply by a tunneling correction
- To do the conventional TST calculation:
  - 1) Find geometry that minimizes  $V(R)$  for reactants and TS (usually a saddle point), typically with a DFT calculation.
  - 2) Compute  $V(R)$  and the 2<sup>nd</sup> derivatives  $\partial^2 V / \partial R_m \partial R_n$  at those two special geometries as accurately as you can afford.
  - 3) Plug those numbers into the TST / stat mech formulas and you probably have a pretty good estimate of  $k(T)$ !

## Reaction Path Degeneracies

Multiply partition function by

$$\frac{m}{\sigma}$$

$m$  = number of optical isomers

$\sigma$  = rotational degeneracy of given configuration

Do for both reactants and transition state

Yields correction to rate constant that is equal to the reaction path degeneracy

Note that this symmetry number includes Symmetrical internal rotors as well as overall Rotations (“external rotors”). Sometimes the Internal and external rotor symmetry numbers are lumped in with  $q_{\text{rot}}$ , don’t double count!

$$\frac{m^{\pm} \sigma}{m \sigma^{\pm}}$$

# A consistency check

- Assuming TST formula is correct:

$$k_{\text{forward}} = k_B T / h \cdot Q^\ddagger / Q_{\text{react}} \exp(-(E_{o,\text{TS}} - E_{o,\text{react}}) / k_B T)$$

$$k_{\text{reverse}} = k_B T / h \cdot Q^\ddagger / Q_{\text{prod}} \exp(-(E_{o,\text{TS}} - E_{o,\text{prod}}) / k_B T)$$

$$\text{So } K_c = k_{\text{forward}} / k_{\text{reverse}} = Q_{\text{prod}} / Q_{\text{react}} \exp(-(E_{o,\text{prod}} - E_{o,\text{react}}) / k_B T)$$

Exactly same thing one gets from Stat Mech Thermo...so at least this rate formula is consistent!

# Homework Question

- Consider the reaction  $\text{C}_6\text{H}_7$  (cyclohexadienyl)  $\rightarrow$   $\text{C}_6\text{H}_6$ (Benzene) + H
- Gao et al. J.Phys.Chem.A (2009) determined the  $\Delta H$  for this reaction is 322 kJ/mole. Tsang J.Phys.Chem.(1986) estimated the entropy of formation of  $\text{C}_6\text{H}_7$  is about 375 J/mole-K at 550 K.
- To a first approximation, the  $Q$ 's for the TS and for the reactant are about the same. Making this approximation, and using Gao and Tsang's numbers, what is  $k(T)$  for this reaction at  $T=550$  K? What are the units?
- Does this reaction follow the Arrhenius rate law  $k(T)=A \exp(-E_a/RT)$ ? Sketch what  $k(T)$  looks like on an Arrhenius plot ( $\ln k$  vs.  $1000/T$ ).
- Compute the reverse rate coefficient, for H atom adding to Benzene at 550 K. What are the units?

## Microcanonical TST: The RRKM rate expression $k(E)$

- The TST equation above assumes a perfect thermal Boltzmann population with a clear temperature  $T$ :  $k(T)$
- In many combustion reactions, the reactions are so fast that a Boltzmann distribution cannot be established. For those cases it is better to use  $k(E)$ , and average as necessary over the true energy distribution.
- The derivation above repeated for microcanonical case gives

$$k(E) = N^\ddagger(E)/h\rho_{\text{reac}}(E)$$

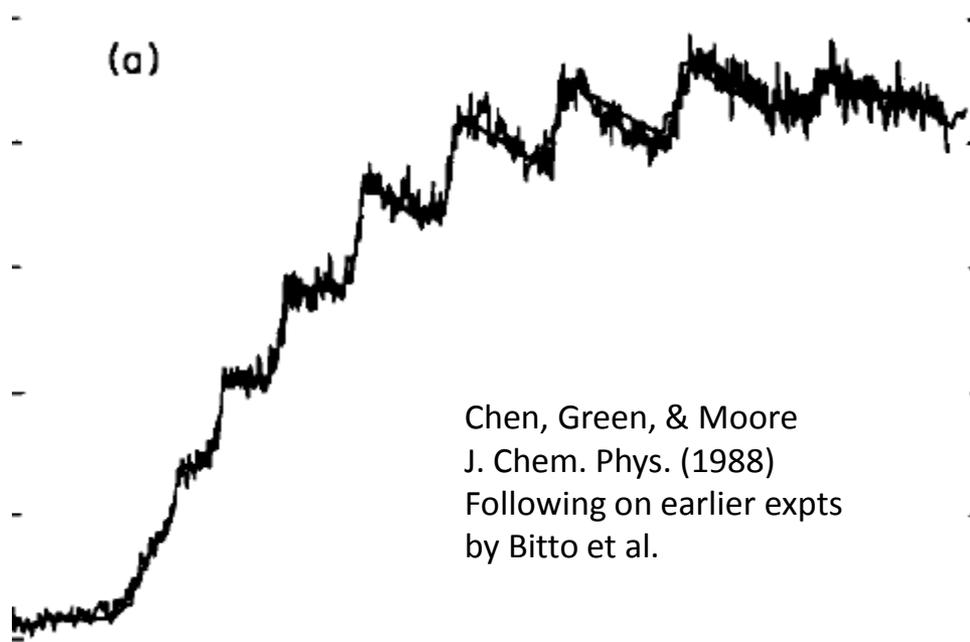
where  $N(E) = \sum \Theta(E - E_i)$  and  $\rho = dN/dE$  Probably Wigner knew this formula.

Rudy Marcus derived this following on work by Rice, Ramsberger and Kassel, who had derived a different equation called RRK, so the new equation is called RRKM. There was a big controversy about this equation for several decades, and competing formulas for  $k(E)$  were proposed.

Note that as written  $N(E)$  is not smooth, it jumps up when  $E$  is high enough to include one more  $E_i$  in the summation. **This was never observed....**

...until the 1980's, when the quantum steps were observed in the reaction  $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$

- Y axis is the Yield of a particular state of  $\text{CH}_2$
- X axis is E
- The Yield is a fraction; numerator  $\sim k(E)$  and denominator is smoothly increasing with E



Now everyone believes  $k(E) = N^\ddagger(E)/h\rho_{\text{react}}(E)$

- W.H. Miller has derived the exact quantum mechanical operator for  $N$ , including tunneling etc. and shown it gives  $k(E)$ . The exact  $N$  gives steps rounded off a bit by tunneling.

- A Boltzmann average of  $k(E)$  gives  $k(T)$  as expected

$$\begin{aligned}k(T) &= 1/Q_{\text{react}} \int \rho_{\text{react}}(E) k(E) \exp(-E/k_B T) dE \\ &= 1/hQ_{\text{react}} \int N^\ddagger(E) \exp(-E/k_B T) dE \quad \text{integrate by parts} \\ &= k_B T/hQ_{\text{react}} \int \rho_{\text{TS}}(E) \exp(-E/k_B T) dE = k_B T/h Q^\ddagger/Q_{\text{react}} \exp(-\beta\Delta E)\end{aligned}$$

- Microcanonical detailed balance:

$$\rho_{\text{react}}(E) k_{\text{forward}}(E) = \rho_{\text{prod}}(E) k_{\text{reverse}}(E) \quad (= N(E)/h)$$

## Number of States

$$N(E, J) = \sum_{i, K} \Theta(E - E_{vib_i} - E_{rot_{J, K}})$$

One should keep track of J and other conserved quantum numbers in addition to E. Currently this is not usually done, but it should be.

$$N(E) = \sum_J N(E, J)(2J + 1)$$

$$N(E) = \int d\varepsilon N_{vib}(E - \varepsilon) \rho_{rot}(\varepsilon)$$

$$\rho_{rot}(E) = \frac{\partial N_{rot}(E)}{\partial E} = \frac{2}{\sigma} \left( \frac{E}{B^2 C} \right)^{1/2}$$

### Beyer-Swinehart for $N_{vib}$

$\omega_j$  = vibrational frequency  
for mode j

1.  $N_{vib}(i) = 1$ , for all i
2. For j = 1, n
3. For i =  $\omega_j, m$
4.  $N_{vib}(i) = N_{vib}(i) + N_{vib}(i - \omega_j)$

5. End i loop
  6. End j loop
- There is a variant on this algorithm which makes it easy to include non-harmonic modes. Astholz Troe and Wieters (1979).

Theory of Unimolecular and Recombination Reactions; R. G. Gilbert and S. C. Smith, Blackwell Scientific

# Beyond Conventional RRHO TST Anharmonicities

Separable - With Beyer Swinehart

Sums and Densities of Fully Coupled Anharmonic Vibrational States: A Comparison of Three Practical Methods

T. L. Nguyen, J. R. Barker, J. Phys. Chem. A, 114, 3718-3730 (2010).

Spectroscopic Perturbation Theory

Relate power series expansion of E in quantum numbers  $v_i$  to higher order derivatives of potential

Problems due to resonances and due to turnovers in  $E(v_i)$

Monte Carlo

$$Q = \int dq_1 \dots dq_n \exp[-\beta V(q_1, \dots, q_n)]$$

Pitzer-Gwinn

$$Q_{\text{quantum,HR}} = Q_{\text{quantum,HO}} * Q_{\text{class,HR}} / Q_{\text{class,HO}}$$

Path Integrals

V. A. Lynch, S. L. Mielke, D. G. Truhlar, J. Chem. Phys. 121, 5148 (2004)

VibSCF; VibCI - MULTIMODE - Bowman

<http://www.chemistry.emory.edu/faculty/bowman/multimode/>

## Beyond Conventional RRHO TST

## Torsions

### Moments of Inertia - Coupling of external and internal momenta

A. L. L. East, L. Radom, J. Chem. Phys. 106, 6655 (1997).

### Torsional Modes - Hindered Rotors

$$Q \sim \int d\phi \exp[-V(\phi)/k_B T]$$

### Pitzer-Gwinn

### Nonseparability of multiple torsional modes

### Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors

S. Sharma, S. Raman, and W. H. Green, J. Phys. Chem. A, 114, 5689-5701 (2010).

### An extended hindered rotor model with incorporation of Coriolis and vibration-rotational coupling for calculating partition functions and derived quantities

P. Vansteenkiste, D. Van Neck, V. Van Speybroeck, and M. Waroquier, J. Chem. Phys. 124, 044314 (2006).

### How should we calculate multi-dimensional potential energy surfaces for an accurate reproduction of partition functions?

P. Vansteenkiste, V. Van Speybroeck, E. Pauwels, and M. Waroquier, Chem. Phys. Lett. 314 109-117, (2006).

See also recent papers by Truhlar on a way to handle coupled torsions. This problem is not completely resolved

# Beyond Conventional RRHO TST

## Variational Transition State Theory

Follow reaction path - Imaginary mode at saddle point

W. L. Hase

D. G. Truhlar

W. H. Miller

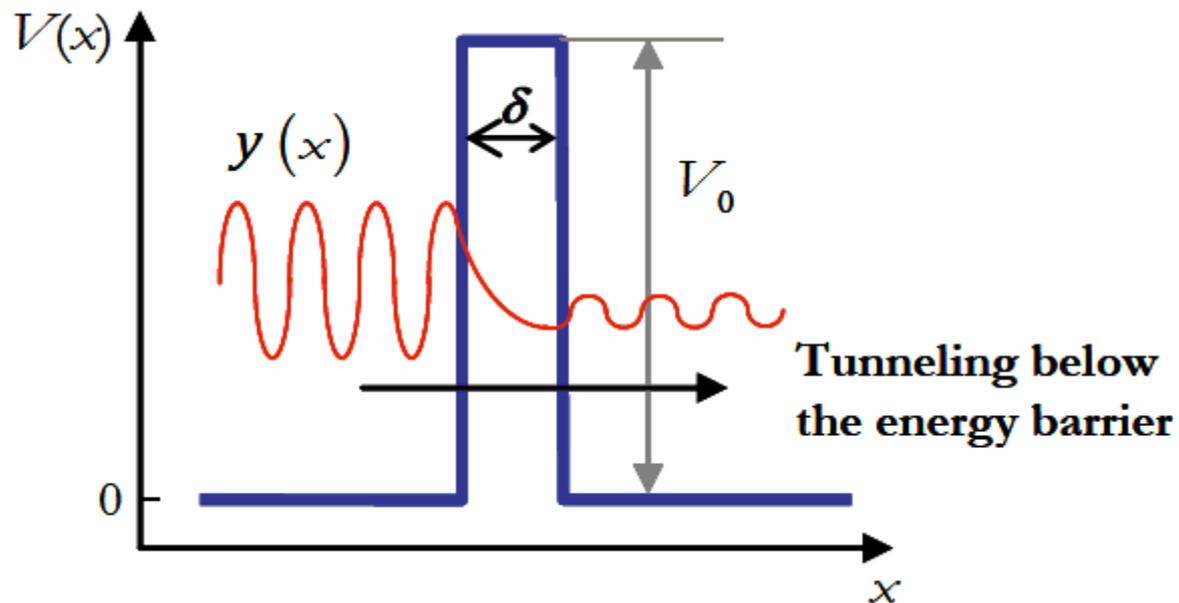
Project vibrational frequencies along reaction path

Evaluate TS partition function along reaction path;

Find minimum

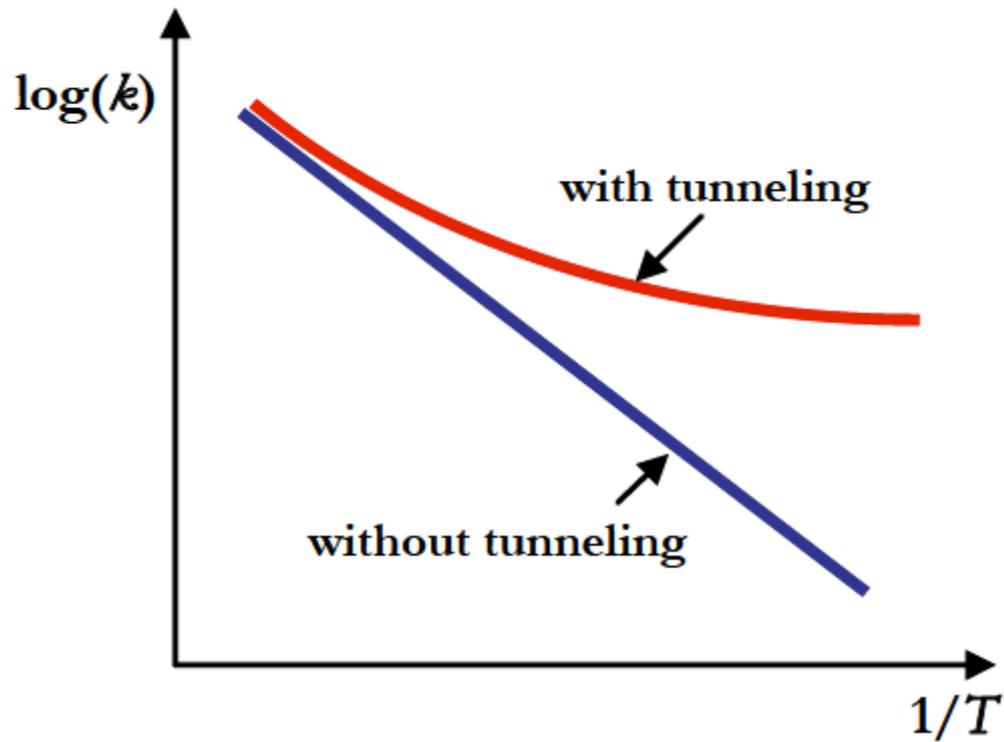
- Canonical -  $k(T) = \min \left\{ \int dE dJ P(E,J) k(E,J,R); R \right\}$
- Microcanonical -  $k(T) = \int dE P(E) \min \left\{ \int dJ P(J) k(E,J,R); R \right\}$
- E, J Resolved -  $k(T) = \int dE dJ P(E,J) \min \left\{ k(E,J,R); R \right\}$

# Quantum Mechanically, you don't need to get over the Barrier You can Tunnel Through the Barrier



A way to beat Arrhenius / Boltzmann restriction on reaction rates

Tunnelling is very important at low T



# Beyond Conventional RRHO TST

## Tunneling Corrections ( $\Gamma$ )

Most Important - Calculate Imaginary Frequency Accurately

### One Dimensional

Wigner - Perturbative Expansion

$$\Gamma = 1 - (\hbar \nu / k_B T)^2 / 24$$

Eckart - Asymmetric form parametrized by reactant, product and saddle point energies

Analytic form for  $\Gamma$

### Multidimensional and Corner Cutting

Small Curvature (SCT)

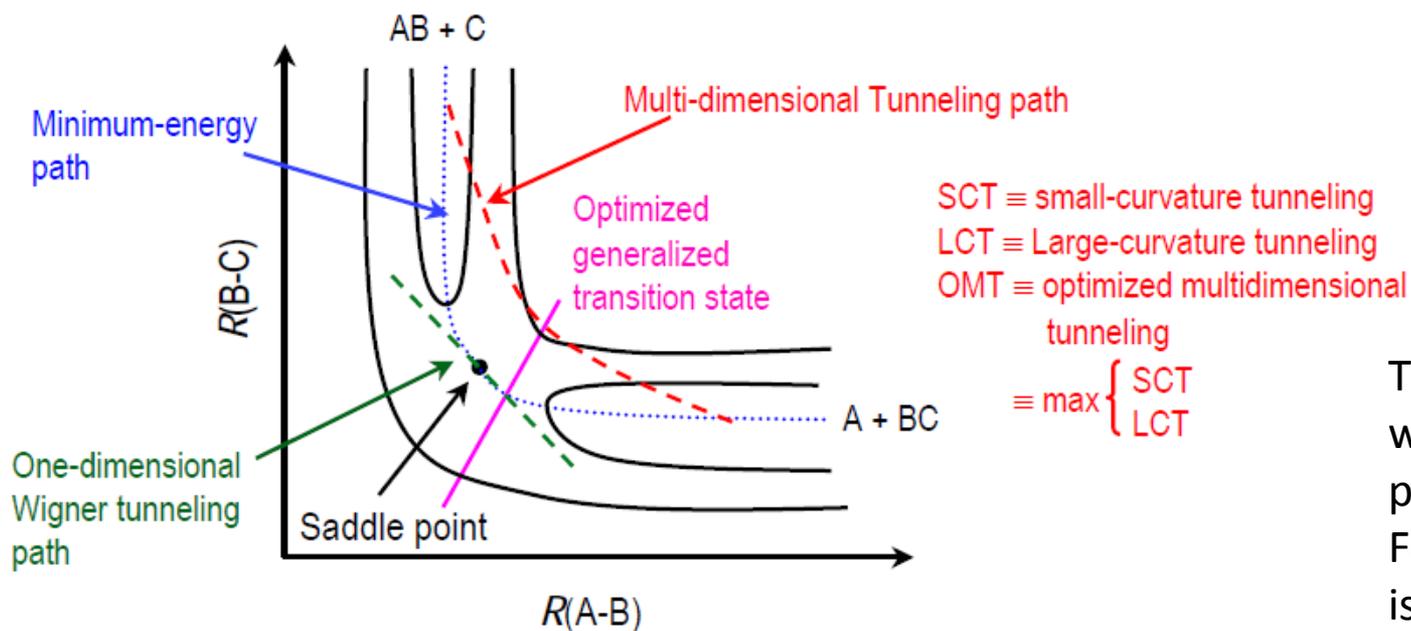
Large Curvature (LCT)

Optimized Multidimensional Tunneling (OMT)

Polyrate - Freeware

<http://comp.chem.umn.edu/polyrate/>

## Variational transition state theory with multi-dimensional tunneling<sup>[1]</sup>



This is another issue which is only partially resolved. Fortunately tunneling is rarely important at combustion T. Extremely important at low T.

[1] For example, see reviews:

Truhlar, Garrett, and Klippenstein *J. Phys. Chem.* **1996**, *100*, 12771.

Fernandez-Ramos, Ellingson, Garrett, and Truhlar, *Rev. Comp. Chem.* **2007**, *23*, 125.

# Summary of Rate Theory

- Almost all methods start from Born-Oppenheimer  $V(R)$ 
  - Crucially depend on accuracy of the (approximate)  $V(R)$
  - Errors in  $V(R)$  directly lead to errors in  $E_a$ , can give big errors.
  - Modern methods can achieve pretty accurate reaction barriers (but not always)
- Classical Mechanics Rate Theory can be transformed into Quantum Mechanics, but exact quantum mechanics usually too hard to solve
- Some simple approximations convert Classical Mechanics into Conventional Transition State Theory, which is much much less expensive to compute. Requires  $V(R)$  at only two points.
  - With reasonable  $V(R)$  almost always gives  $k(T)$  within order of magnitude of true value. Sometimes better than factor of 2.
- Several of the simple approximations in Conventional Transition State Theory are not quite good enough, give small but significant errors. Improved approximations are under development.

# Some important Qualitative differences between PES's for different reactions

