

Topic 4

Thermodynamics

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

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

Hess's Law:

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the reaction may be divided

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

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

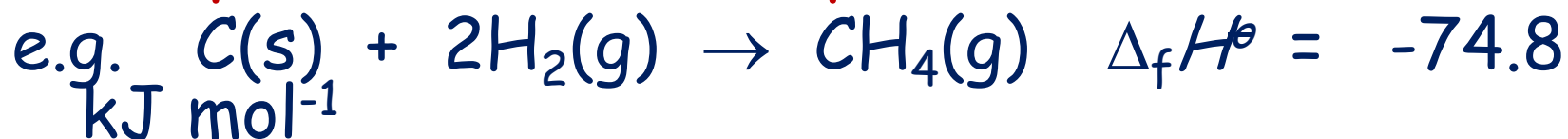
$$K = \frac{\prod_{\text{products}} (a_i^{v_i})}{\prod_{\text{reactants}} (a_i^{v_i})}$$

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 H₂(g) are both zero

The reference state for carbon is graphite.

Standard entropy

Standard entropy

Based on the 3rd law of

Thermodynamics:

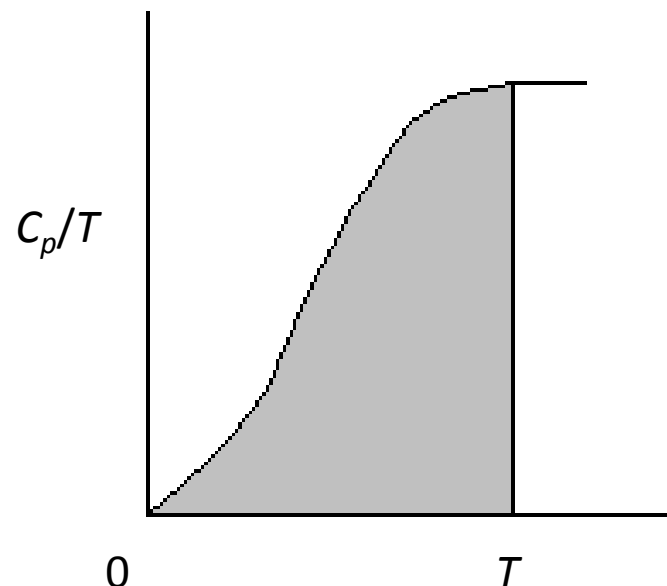
The entropy of any perfectly crystalline material at $T = 0$ is zero

Standard molar entropy, S_m^\ominus

The entropy of 1 mol of a substance in its standard state based on the 3rd 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

Molecular partition functions: rigid rotor harmonic oscillator (RRHO) - a reminder

$$q_{total} = q_{trans} q_{rot} q_{vib} q_{elect}$$

$$q_{trans} = \left[\frac{2\pi m k T}{h^2} \right]^{3/2} V$$

$$Q = q/V$$

$$q_{rot} = \frac{kT}{\sigma h B c}$$

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left\{ \frac{(\frac{kT}{hc})^3}{ABC} \right\}^{1/2}$$

$$q_{vib} = (1 - e^{-\frac{hc\omega}{kT}})^{-1}$$

$$q_{vib} = \prod_{i=1}^{\alpha} (1 - e^{-\frac{hc\omega_i}{kT}})^{-1}$$

$$q_{elect} = \sum_{levels, i} g_i e^{-\beta \epsilon_i}$$

These expressions allow thermodynamic data to be calculated from spectroscopic data and from electronic structure calculations

Thermodynamic quantities from partition functions

$$U = U(0) - N \left(\frac{\partial \ln q}{\partial \beta} \right)_V = U(0) + NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

$$\beta = \frac{1}{kT} \quad U(0) = N_A \varepsilon_0$$

$$S = \frac{U - U(0)}{T} + R \ln q - R \ln N_A + R$$

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_V ; \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p \\ &= C_V + R \text{ (ideal gas)} \end{aligned}$$

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 ⁻¹	Review	Chase 1998
$\Delta_f H^\ominus$	-74.6±0.3	kJ mol ⁻¹	Review	Manion
S^\ominus	188.66±0.42	J mol ⁻¹ K ⁻¹	N/A	Colwell 1963

Sym. Species	No	Approximate type of mode	Selected Freq. Value Rating	Infrared Value Phase	Raman Value Phase	Comments
a ₁	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 v ₄
f ₂	3	Deg str	3019 A	3018.9 gas	3019.5	
f ₂	4	Deg deform	1306 C	1306.2 gas		

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

- The CCCBDB contains links to experimental and computational thermochemical data for a large selected set of **gas-phase** atoms and molecules. Tools for comparing experimental and computational ideal-gas thermochemical properties
- **Species in the CCCBDB**
 - Mostly compounds with atoms with atomic number less 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

Computed data

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



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

Frequency in 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

Methane

HF/6-31G*

Frequency in cm^{-1}

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

The calculated vibrational frequencies were scaled by 0.8985

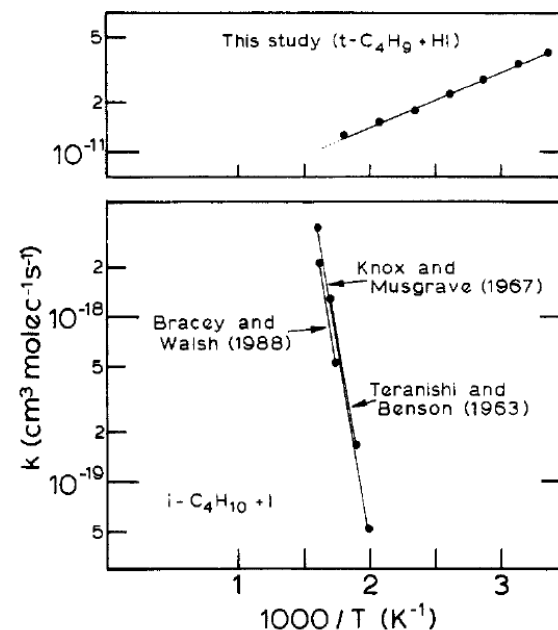
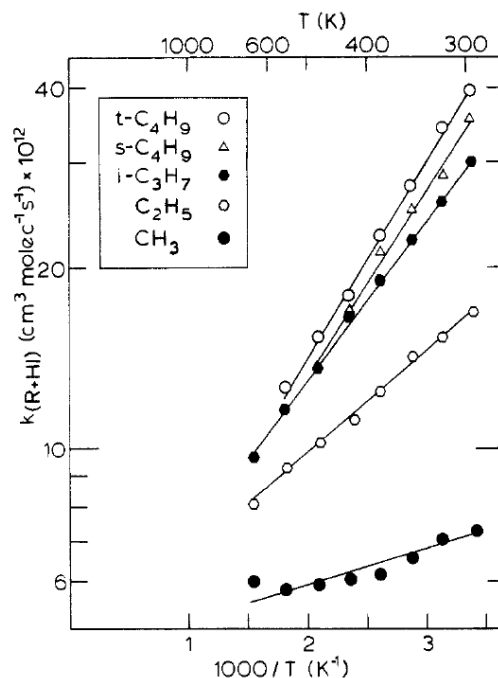
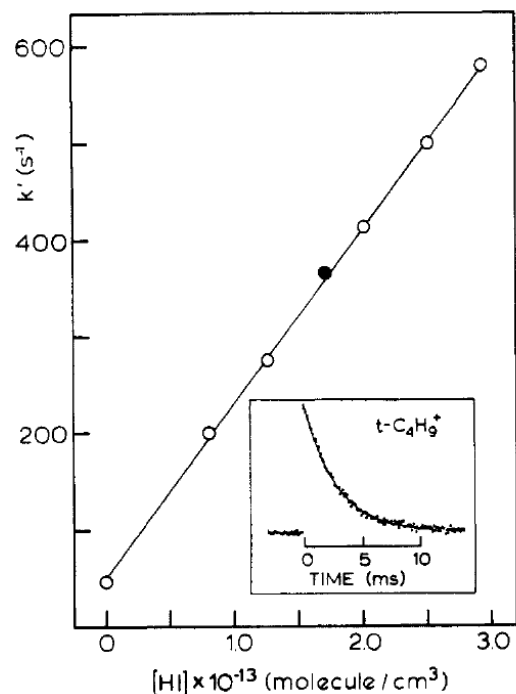
Enthalpies of formation of radicals

- 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: CH_3 . Determined by:
 - Kinetics, e.g. J Am Chem Soc, 1990, 112, 1347
 - Photionization spectroscopy, e.g. J Chem Phys, 1997, 107, 9852
 - Electronic structure calculations, e.g. J Chem Phys, 2001, 114, 6014
- Recommended value by IUPAC: $\Delta_f H^\circ(298.15 \text{ K}) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$

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

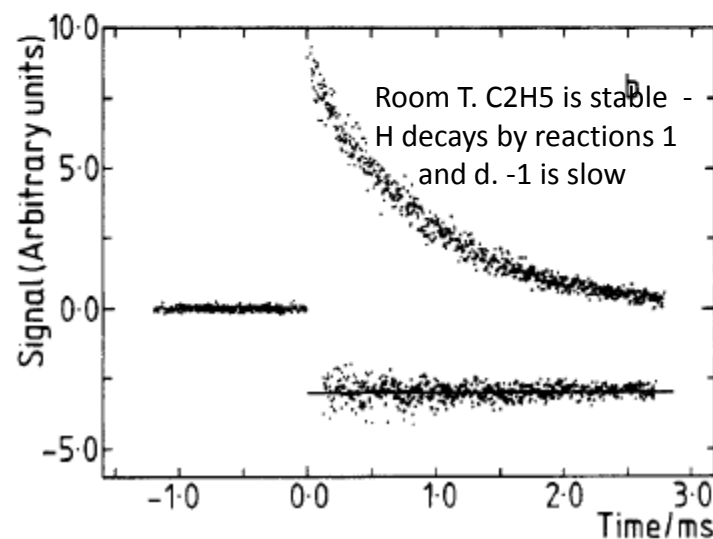
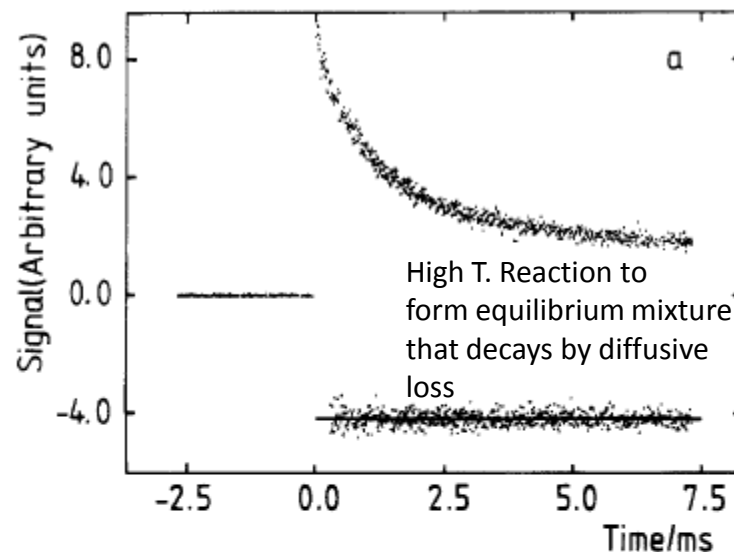


Direct measurement of equilibrium constant for reactions involving radicals: $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$

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



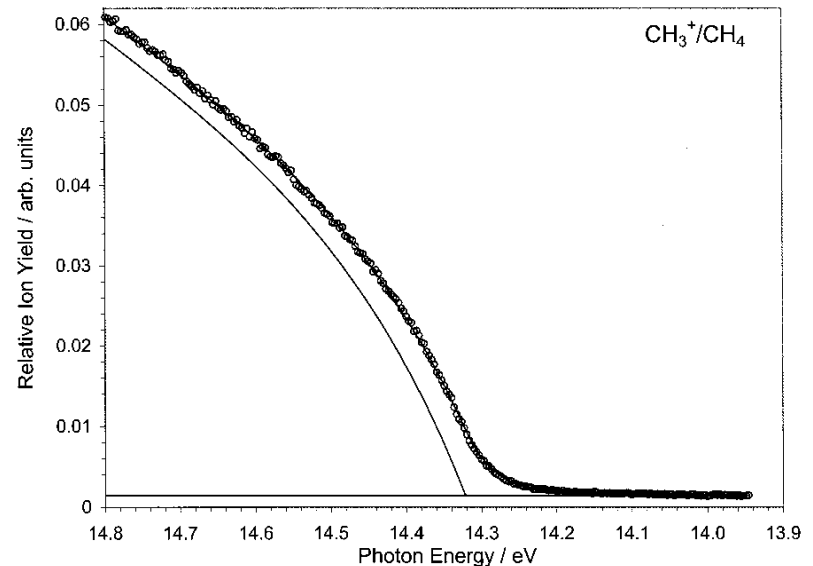
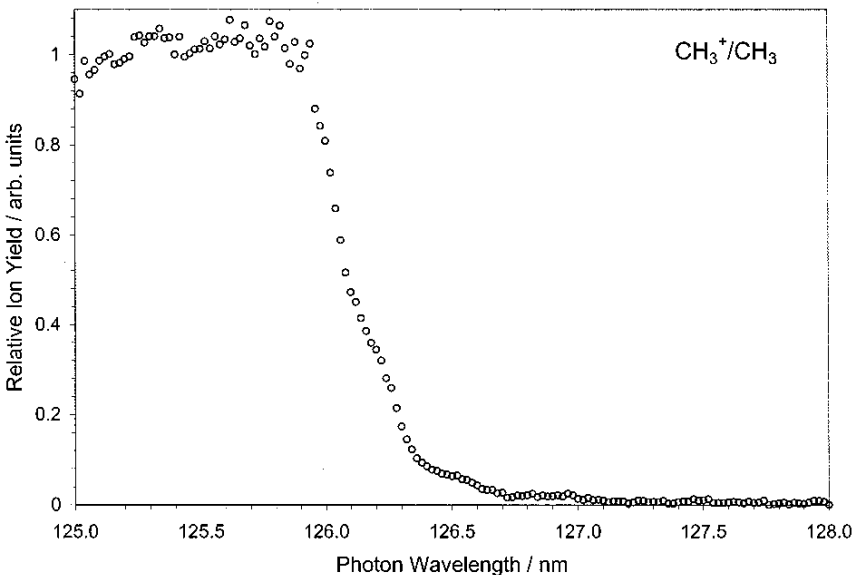
- Solve rate equations - gives bi-exponential decay of H, k_1 and k_{-1} and hence K_1 from analysis. Vary T, enthalpy of reaction from second or third law.



Photoionization spectrum of CH_3

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

- Mesaure the photionization threshold for CH_3 and the appearance potential of CH_3^+ from CH_4 photexcitation. Obtain the dissociation energy of $\text{CH}_3\text{-H}$:



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 $\text{R-H} \rightarrow \text{R} + \text{H}$:

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

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

$$D_0(\text{R-H}) = E_0(\text{R}) + E_0(\text{H}) - E_0(\text{RH})$$

- Bond energies can be converted to bond enthalpy changes using the relation $U = H + pV = H + RT$, so that, for $\text{R-H} \rightarrow \text{R} + \text{H}$, $\Delta U = \Delta H + RT$. 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

Active Thermochemical Tables

<https://atct.anl.gov/>

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Active Thermochemical Tables - X

https://atct.anl.gov

active thermochemical tables

Argonne NATIONAL LABORATORY

ACTIVE THERMOCHEMICAL TABLES

ATcT

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Welcome to the ATcT website!

Active Thermochemical Tables (ATcT) are a new paradigm of how to develop accurate, reliable, and internally consistent thermochemical values (such as enthalpies of formation, Gibbs energies of formation, bond dissociation energies, reaction enthalpies, etc.) for stable, reactive, and transient chemical species by utilizing to the fullest all available experimental measurements as well as state-of-the-art theoretical data. As opposed to traditional sequential thermochemistry (A begets B, which begets C, etc.), ATcT is based on constructing, analyzing, and solving the underlying Thermochemical Network (TN). The ATcT approach propels thermochemistry to a new orbit by rectifying fundamental deficiencies ingrained in the traditional approach to thermochemistry. It also acts as a unique bridge that efficiently interfaces experiments and theory and integrates the best aspects of both. Finally, ATcT introduces to thermochemistry a number of entirely new capabilities that were never available before.

The latest released version (TN 1.122) continues to include a **find** functionality, as well as a **provenance analysis** of the enthalpy of formation of each of the ~1200 species (except the elements in their standard states), accessible by clicking on the species name.

The species-specific page now includes a number of new features, such as a **3D depiction of the target species**, a list of **other highly correlated enthalpies of formation**, as well as a list of **most influential determinations including the target species**.

Another new feature is the ability to **calculate 0 K and 298.15 K reaction enthalpies, bond dissociation enthalpies, gas-phase acidities, proton affinities, etc.** on the fly, accessible by clicking the 'Reaction Search' at the bottom of the yellow Find Bar.

You can check out the thermochemical values by selecting "Thermochemical Data" from the navigation bar above.

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Latest version: <https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php>
1199 species included in version 1.122 (as of 09/05/2016)

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

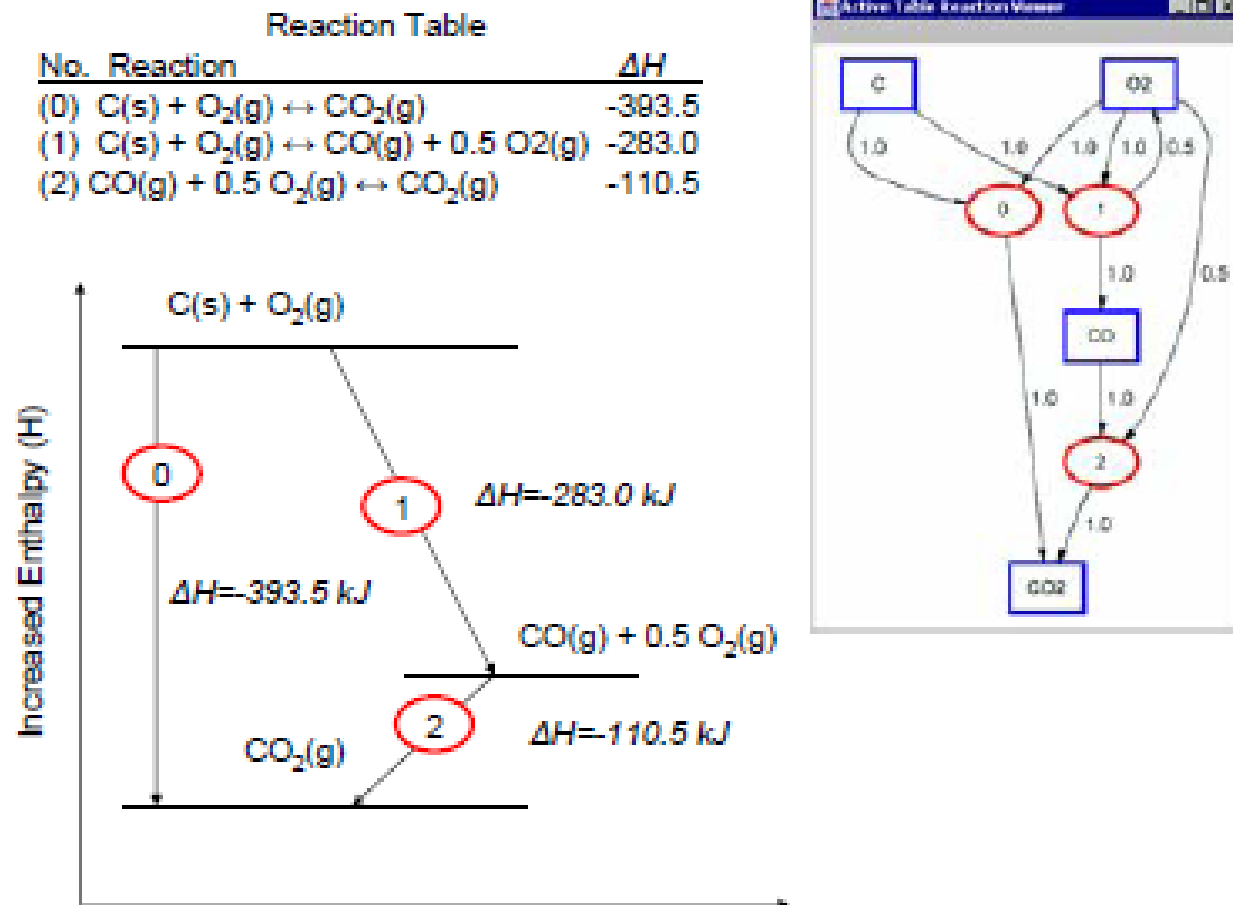


Fig. 1. Enthalpy diagrams and thermochemical reaction tables.

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

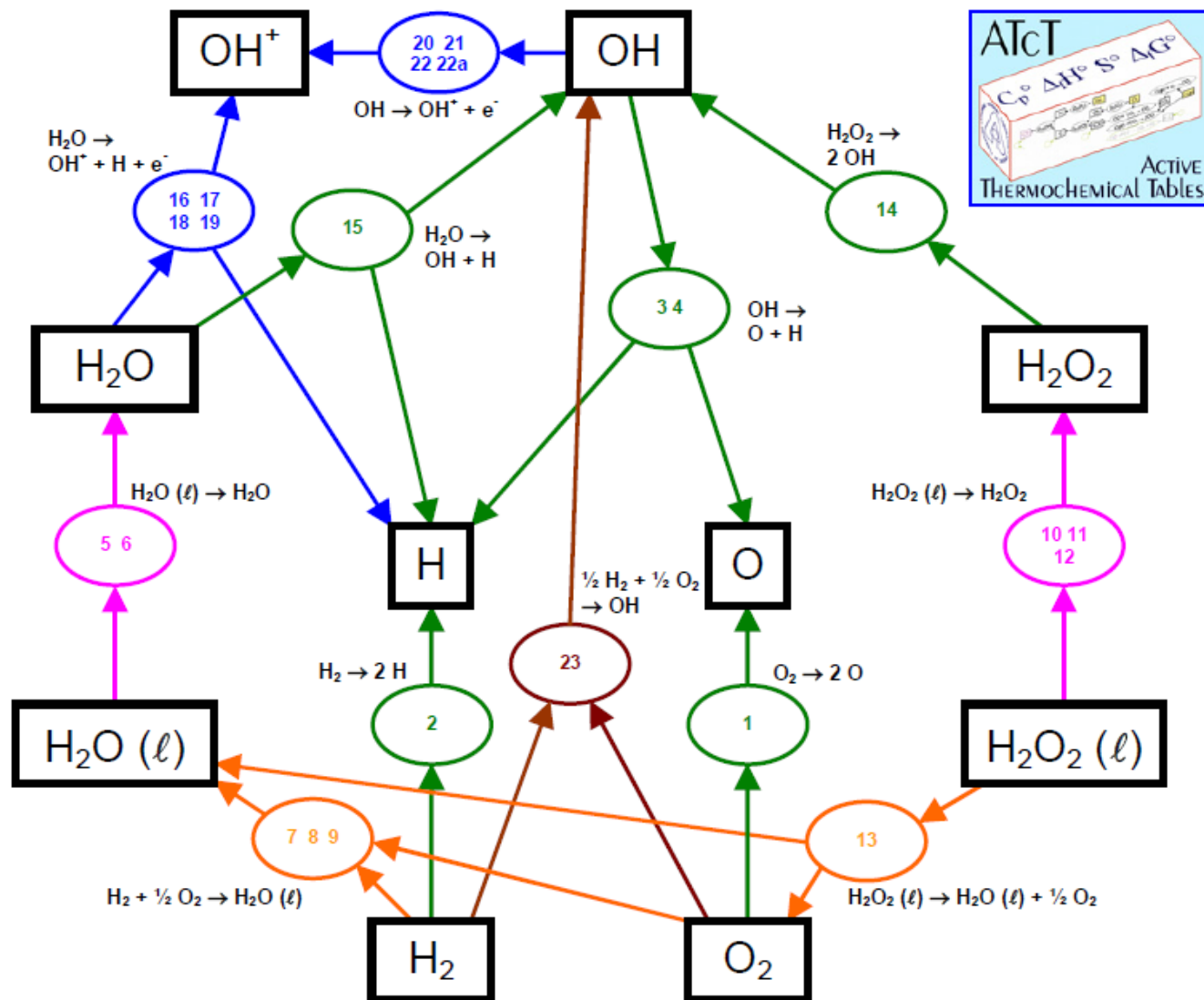
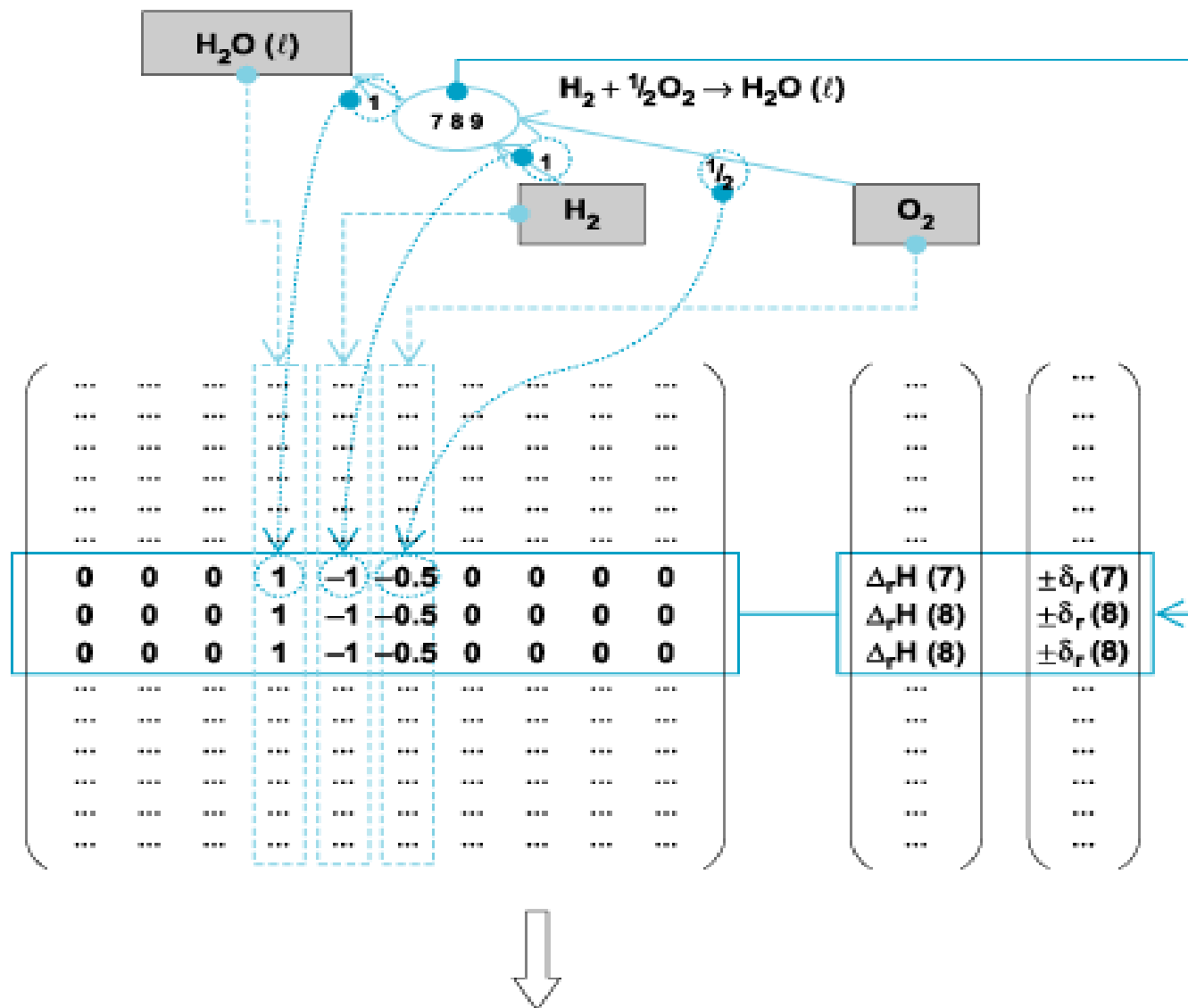


Figure 1. A small subsection of the current Core (Argonne) Thermochemical Network. The full network currently contains >600 primary vertices and >3200 secondary vertices. See text for further details



...

Eq. (7): $\Delta_r H(\text{H}_2\text{O} < l >) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (7) \pm \delta_r (7)$

Eq. (8): $\Delta_r H(\text{H}_2\text{O} < l >) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (8) \pm \delta_r (8)$

Eq. (9): $\Delta_r H(\text{H}_2\text{O} < l >) - \Delta_r H(\text{H}_2) - 0.5 \Delta_r H(\text{O}_2) = \Delta_r H (9) \pm \delta_r (9)$

...

Evidence for a Lower Enthalpy of Formation of Hydroxyl Radical

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

Note that these are values at 0 K
Current ATcT value is
 $8.904 \pm 0.006 \text{ kcal mol}^{-1}$

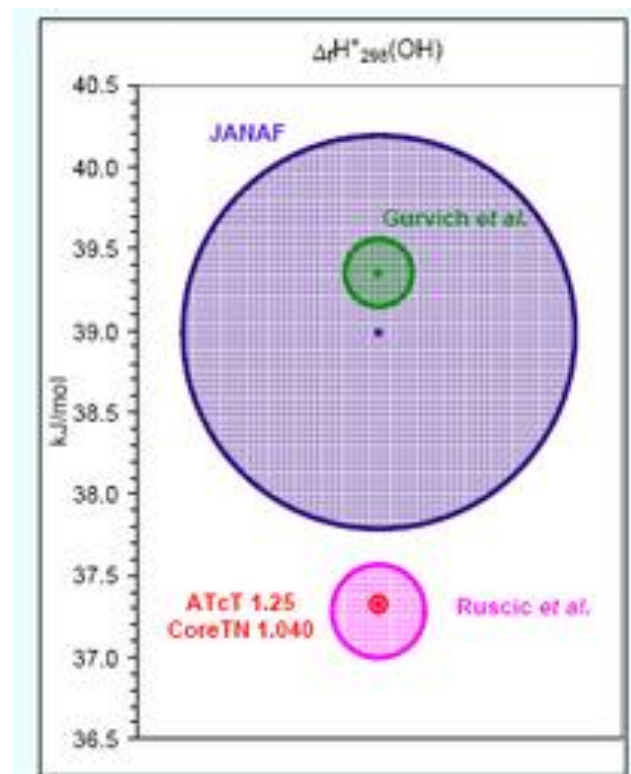


TABLE 1: Various Values for the 0 K Enthalpy of Formation of OH and Related Values for $D_0(\text{H}-\text{OH})$ and $D_0(\text{OH})^a$

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

Example: CH₃

Formula	$\Delta_f H^\circ(0\text{ K})$	$\Delta_f H^\circ(298\text{K})$	Uncertainty	Units
CH ₃ (g)	149.788	146.374	± 0.08	kJ mol ⁻¹

95% uncertainty limits

- Top contributors to the provenance of $\Delta_f H^\circ$ of CH₃ (g):
The top 20 contributors account only for 72.5% of the provenance of $\Delta_f H^\circ$ of CH₃ (g). A total of 99 contributors would be needed to account for 90% of the provenance.
- Link to latest version of ATcT:
<https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php>

Provenance of ATcT determination of the enthalpy of formation of ethyl

- $\Delta_f H^\circ(\text{C}_2\text{H}_5) = 119.86 \pm 0.28 \text{ kJ/mol at } 298.15 \text{ K}$
- See website for provenance

<https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php>

Example of current accuracy in ATcT



- the enthalpy of the reaction is equivalent to the difference in bond dissociation energies of H_2 and CH_2 , and noting that $D_0(\text{CH}_2) = \text{TAE}(\text{CH}_2) - \text{TAE}(\text{CH})$, the recently published ATcT total atomization energies (TAE) for CH_2 and CH and the ATcT enthalpy of formation for H produce a quite accurate 0 K enthalpy of the reaction of 3.36 ± 0.08 kcal/mol (14.04 ± 0.35 kJ/mol). The latest ATcT value is nearly identical, 3.397 ± 0.04 kcal/mol (14.21 ± 0.16 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, based solely on the enthalpy change
- * Note the heavy reliance on theory

Ab Initio Computations and Active Thermochemical Tables Hand in Hand: Heats of Formation of Core Combustion Species

Klippenstein, Harding, Ruscic, J. Phys. Chem. A 2017, 121, 6580-6602

- High level ab initio electronic structure based predictions of $\Delta_f H^\circ(0\text{ K})$ for 348 C, N, O, and H containing species - essentially all core combustion species with 34 or fewer electrons.
- The accuracy of the theoretical predictions is explored through (i) examination of the magnitudes of the various corrections, (ii) comparisons with other high level calculations, and (iii) through comparison with the ATcT values.
- Inclusion of these theoretical results into the ATcT thermochemical network is expected to significantly improve the thermochemical knowledge base for less-well studied species

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.

RESPECTH

Reaction Kinetics, Spectroscopy, Thermodynamics database

- <http://respecth.chem.elte.hu/respecth/>
- Thermodynamics section:
 - thermochemical data calculated by the method NEAT;
 - high-accuracy thermochemical data for $\text{H}_2^{(16)}\text{O}$;
 - A mirror of Burcat's thermochemistry database (see next slide), with species searching and function plotting additions.

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:

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

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

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

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

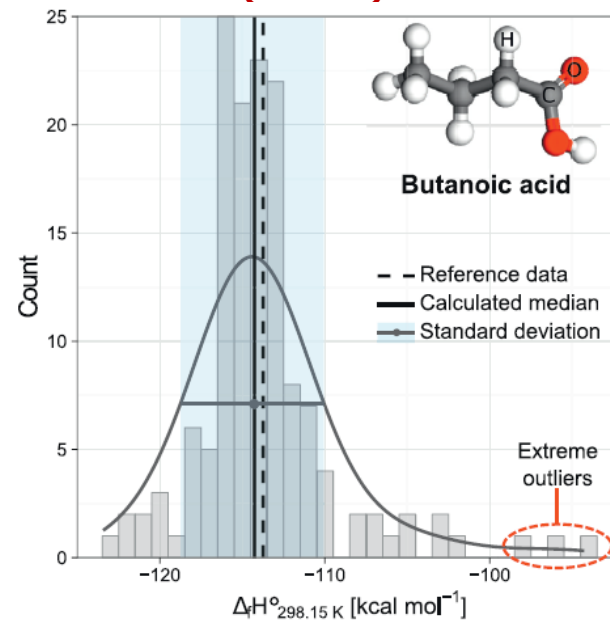
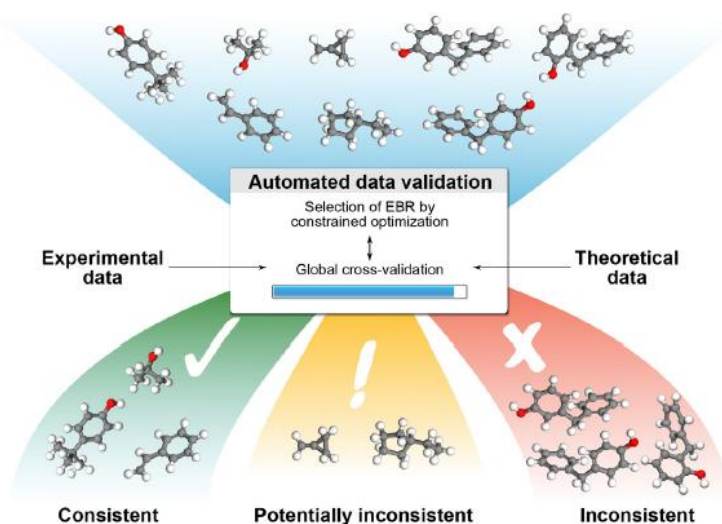
- Linked to ATcT and used in Chemkin.

Burcat database. Entry for CH₃

- 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. 2nd set are
a1-a7 for 200 - 1000 K. Temp ranges specified in line
1

A big data framework to validate thermodynamic data for chemical species

Buerger et al. Combustion and Flame 176 (2017) 584-591



- validate data for the standard enthalpy of formation for 920 gas-phase species containing carbon, oxygen and hydrogen retrieved from the NIST Chemistry WebBook.
- Use error cancelling balanced reactions (specifically isodesmic reactions) to calculate a distribution of possible values for the standard enthalpy of formation of each species.
- method automates the identification and exclusion of inconsistent data
- exploits knowledge of the structural similarities between species and the consistency of the data to identify which species introduce the most error and recommend what future experiments and calculations should be considered

An adaptive distance-based group contribution method for thermodynamic property prediction

He et al., Phys.Chem.Chem.Phys.,2016, 18, 23822

- standard enthalpy of formation (H_f ,298K) for alkanes, alkenes, and their radicals at the M06-2X/def2-TZVP//B3LYP/6-31G(d) level
- Multiple linear regression (MLR) and artificial neural network (ANN) fitting used to obtain the contributions from individual groups and group interactions for further predictions
- characterizes the group interaction within a molecule with an exponential decay function of the group-to-group distance, defined as the number of bonds between the groups
- More accurate than conventional group additivity using same training sets

Exercise 3

The NASA polynomial coefficients, a_1 - a_5 , between 1000 K and 3000 K for N_2 are:

2.95257637E+00 1.39690040E-03 -4.92631603E-07

7.86010195E-11 -4.60755204E-15

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

Calculate the heat capacity over the temperature range 1000 - 3000 K. Calculate the vibrational contribution to the heat capacity given that the translational and rotational contributions are $3R/2$ and R respectively. (Remember $C_p = C_v + R$)

Compare these results from those calculated from statistical mechanics. The vibrational heat capacity is given by:

$$C_v = R\Omega^2 e^{\Omega} / (e^{\Omega} - 1)^2 \quad \text{where } \Omega = \frac{hc\omega}{kT}$$
$$hc/k = 0.659 \text{ cm K}; \quad \omega(N_2) = 2359 \text{ cm}^{-1}$$

Comment on the differences

Reminder

- Look back at slides on Statistical Mechanics:

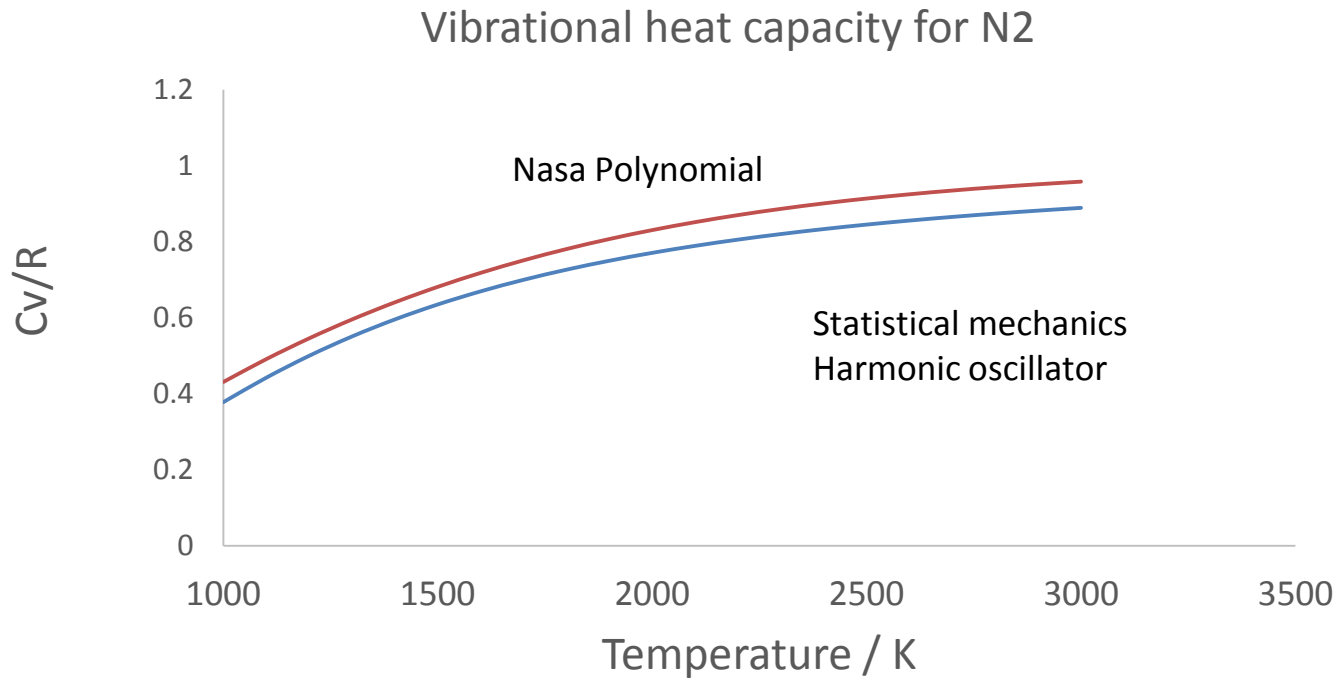
- Translational partition function $q_{trans} = \left[\frac{2\pi mkT}{h^2} \right]^{3/2} V$

- Rotational partition function $q_{rot} = \frac{kT}{\sigma h B c}$

- Energy $U = U(0) - N \left(\frac{\partial \ln q}{\partial \beta} \right)_V = U(0) - N k T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$

- Heat Capacity $C_V = \left(\frac{\partial U}{\partial T} \right)_V$; $C_p = \left(\frac{\partial H}{\partial T} \right)_p$

Exercise 3



NB The statistical mechanics calculation is based on a harmonic oscillator model for N₂. Incorporating anharmonicity will increase the calculated heat capacity