

Thermodynamics

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

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

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

A statement of Hess's Law

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

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

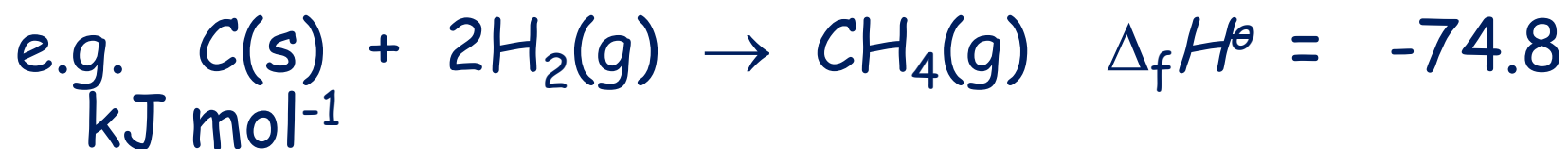
$$RT \ln K = -\Delta G$$

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

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

Standard entropy

Standard entropy

Based on the 3rd law of

Thermodynamics:

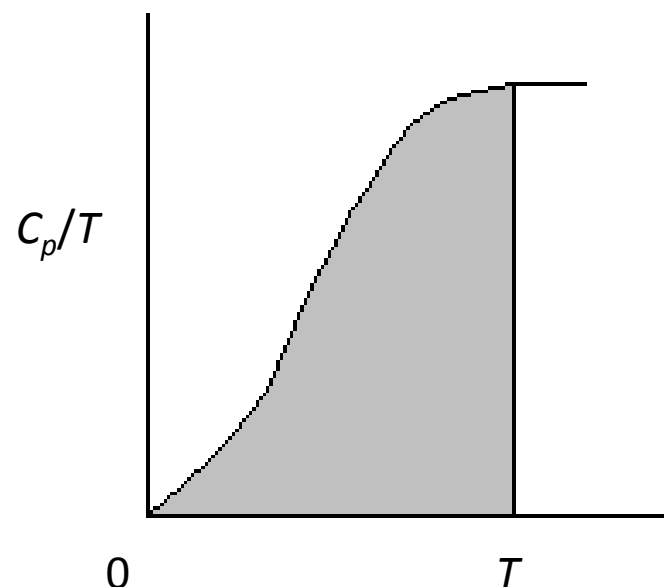
The entropy of any perfectly crystalline material at $T = 0$ is zero

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

Statistical mechanics

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

$$U(T) - U(0) = NkT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V \quad U(0) = N\epsilon_0$$

$$S = \frac{U(T) - U(0)}{T} + Nk(\ln Q - \ln N!)$$

$$C_V = \left(\frac{\partial U(T)}{\partial T}\right)_V ; C_p = C_V + R$$

Canonical Partition Functions

Rigid Rotor Harmonic Oscillator (RRHO) Klippenstein p13

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{elec}$$

$$Q_{trans} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V$$

$$Q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 I_a k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_b k_B T}{h^2} \right)^{1/2} \left(\frac{8\pi^2 I_c k_B T}{h^2} \right)^{1/2}$$

$$Q_{vib}^{quan} = \prod_{i=1}^n \frac{\exp(-h\nu_i / 2k_B T)}{1 - \exp(-h\nu_i / k_B T)} \quad Q_{vib}^{class} = \prod_{i=1}^n \frac{k_B T}{h\nu_i}$$

$$Q_{elec} = \sum_{i=1} g_i \exp\left(-\frac{E_i}{k_B T}\right)$$

These expressions allow entropies and heat capacities to be calculated from spectroscopic data

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 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](#)

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

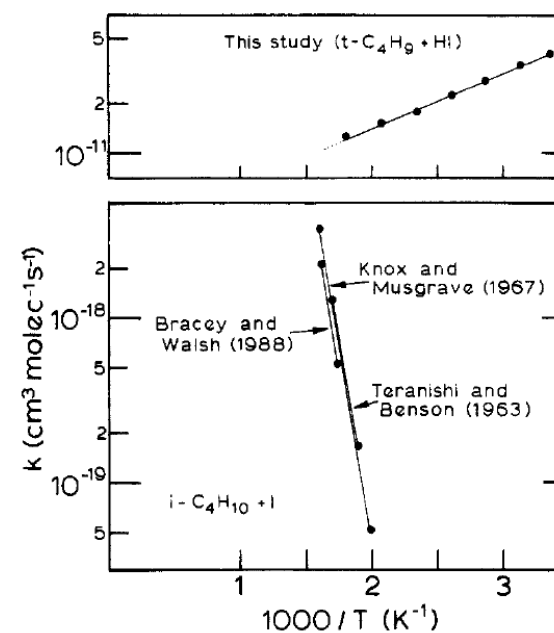
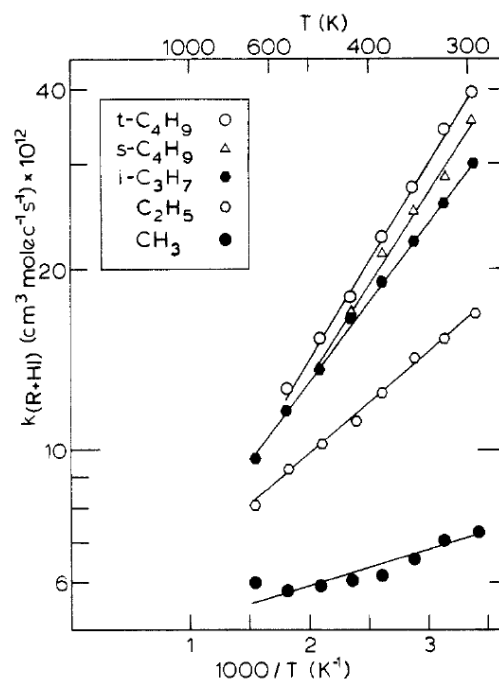
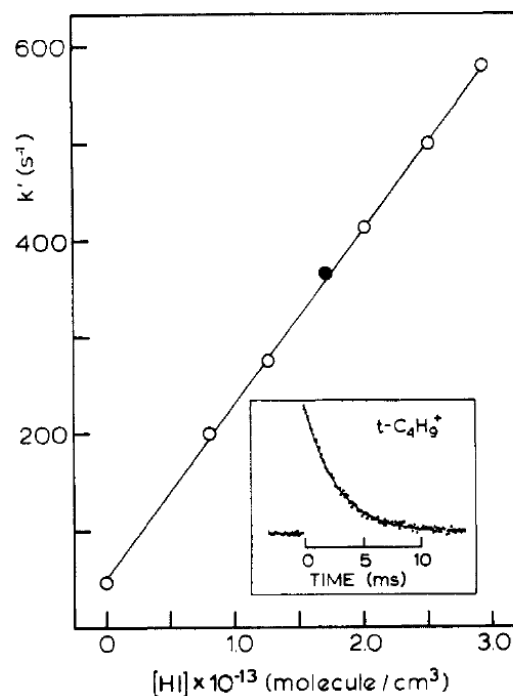
Enthalpies of formation of radicals

- 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: $\Delta_f H^\ominus(298.15 \text{ K}) = 146.7 \pm 0.3 \text{ kJ mol}^{-1}$

Kinetics and thermodynamics of alkyl radicals

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

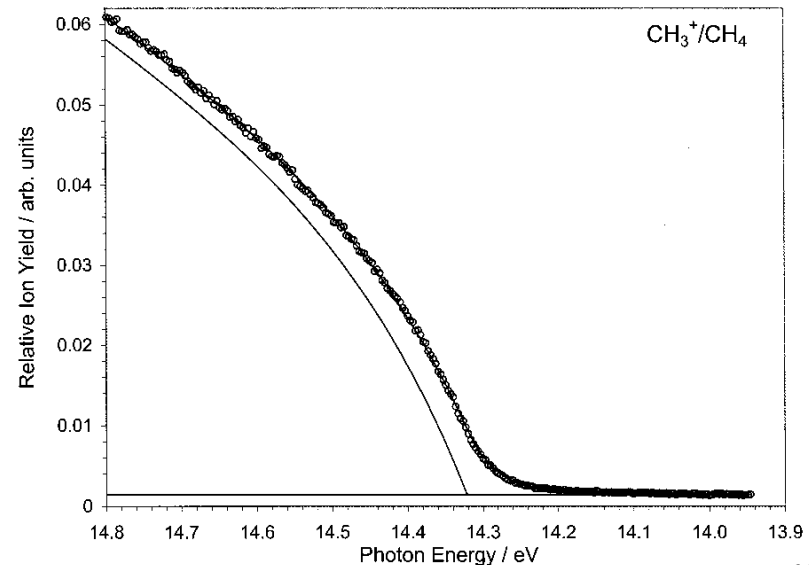
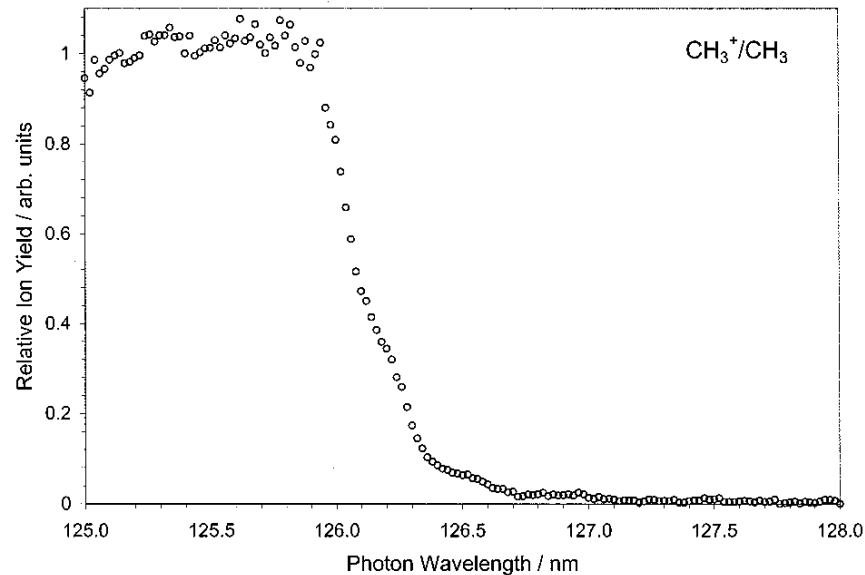
- Measured $k(T)$ for $R + HI$, using laser flash photolysis / photoionization mass spectrometry, and combined with existing data for reverse reaction ($I + RH$) to determine equilibrium constant. Enthalpy of reaction determined by second and third law methods



Photoionization spectrum of CH_3

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

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



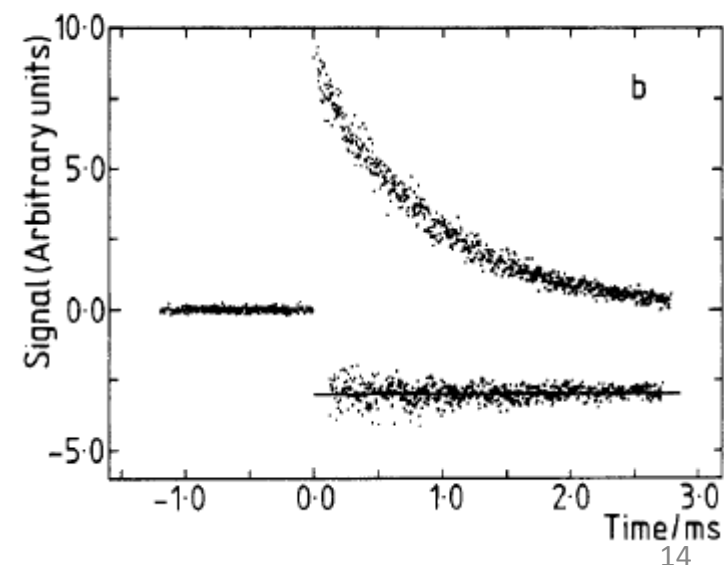
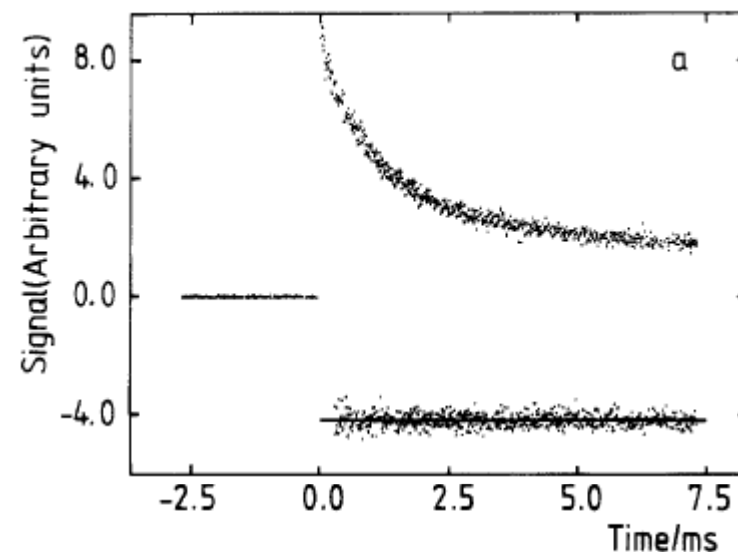
Direct measurement of equilibrium constant for reactions involving radicals: $\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_5$

- 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.



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.

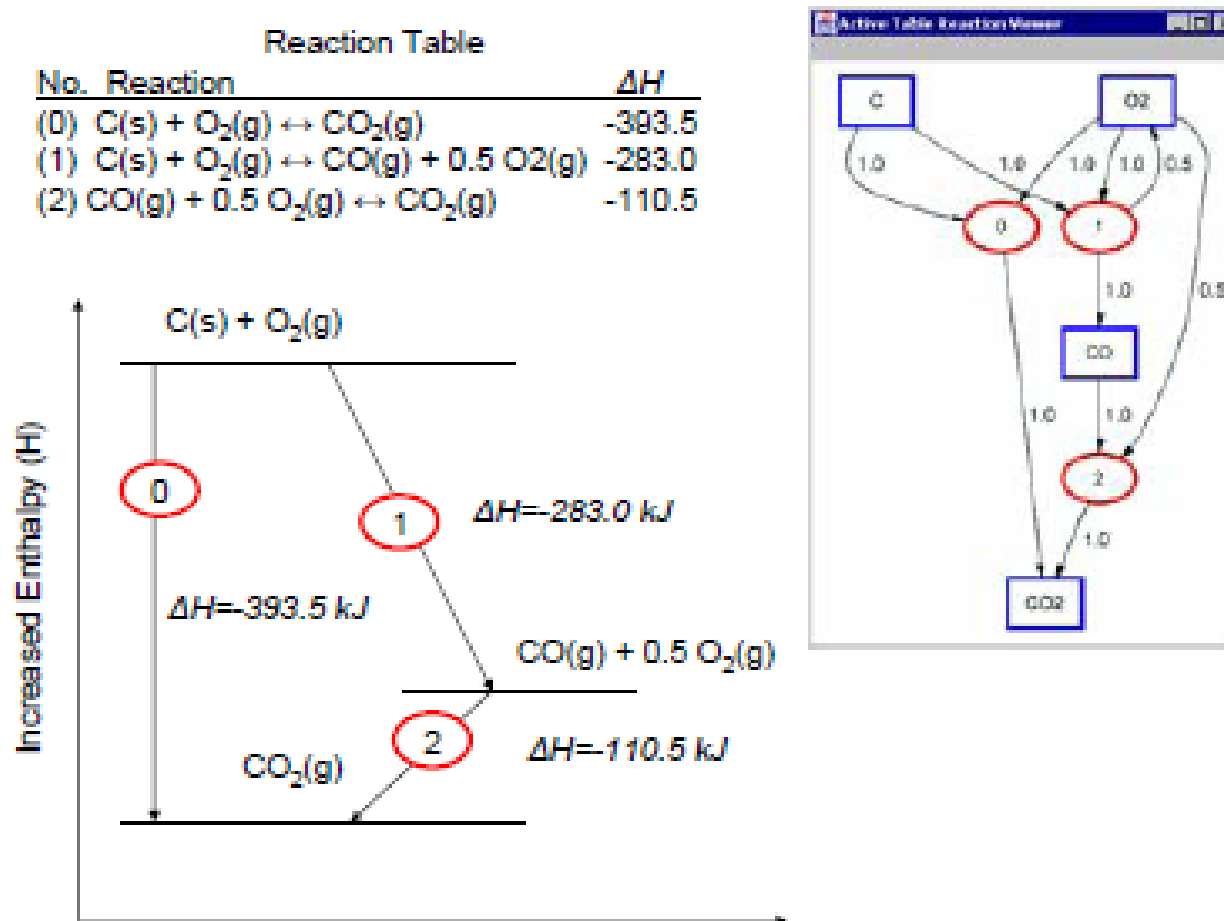


Fig. 1. Enthalpy diagrams and thermochemical reaction tables.

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

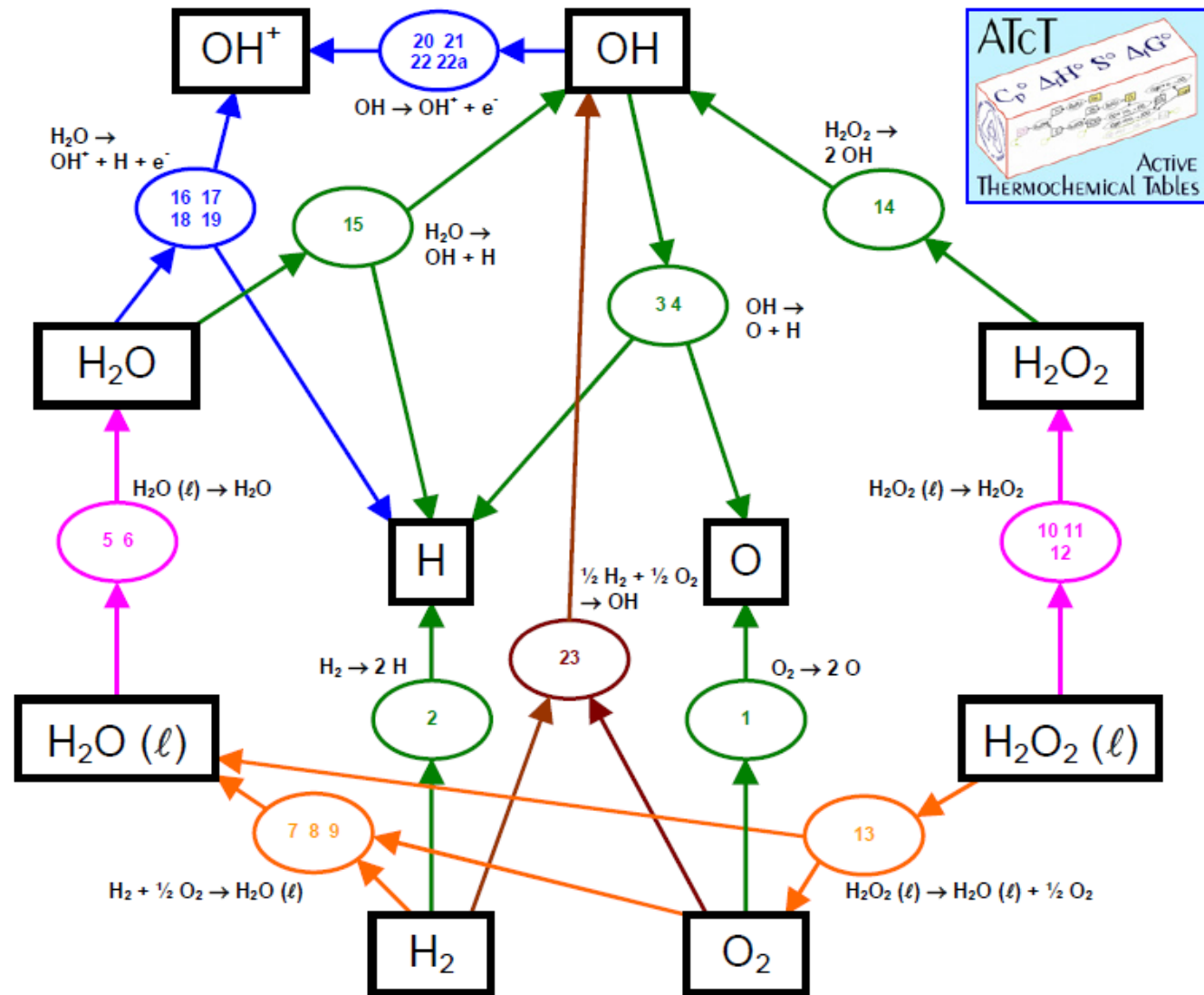


Figure 1. A small subsection of the current Core (Argonne) Thermochemical Network. The full network currently contains >600 primary vertices and >3200 secondary vertices. See text for further details

Evidence for a Lower
Enthalpy of Formation
of Hydroxyl Radical
Ruscic et al. J Phys Chem,
2001, 105, 1

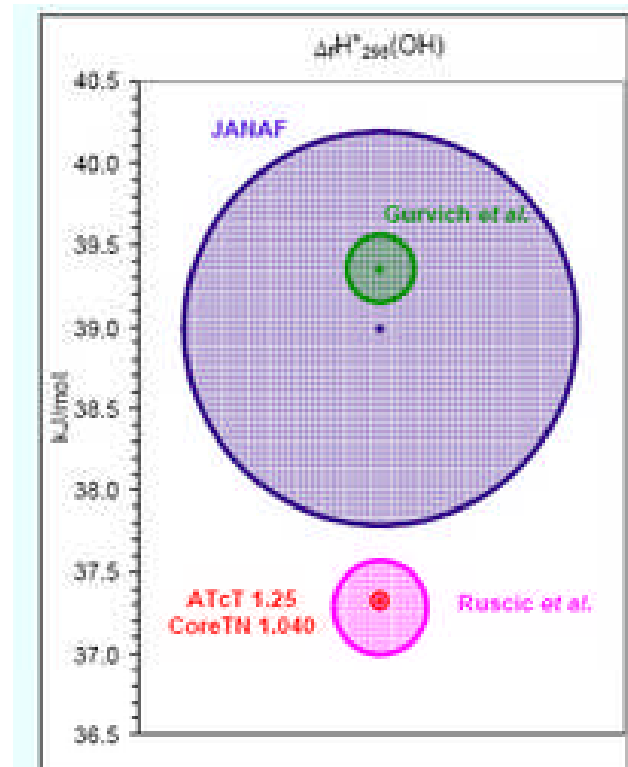


TABLE 1: Various Values for the 0 K Enthalpy of Formation of OH and Related Values for $D_0(\text{H}-\text{OH})$ and $D_0(\text{OH})^a$

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

Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO₂

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

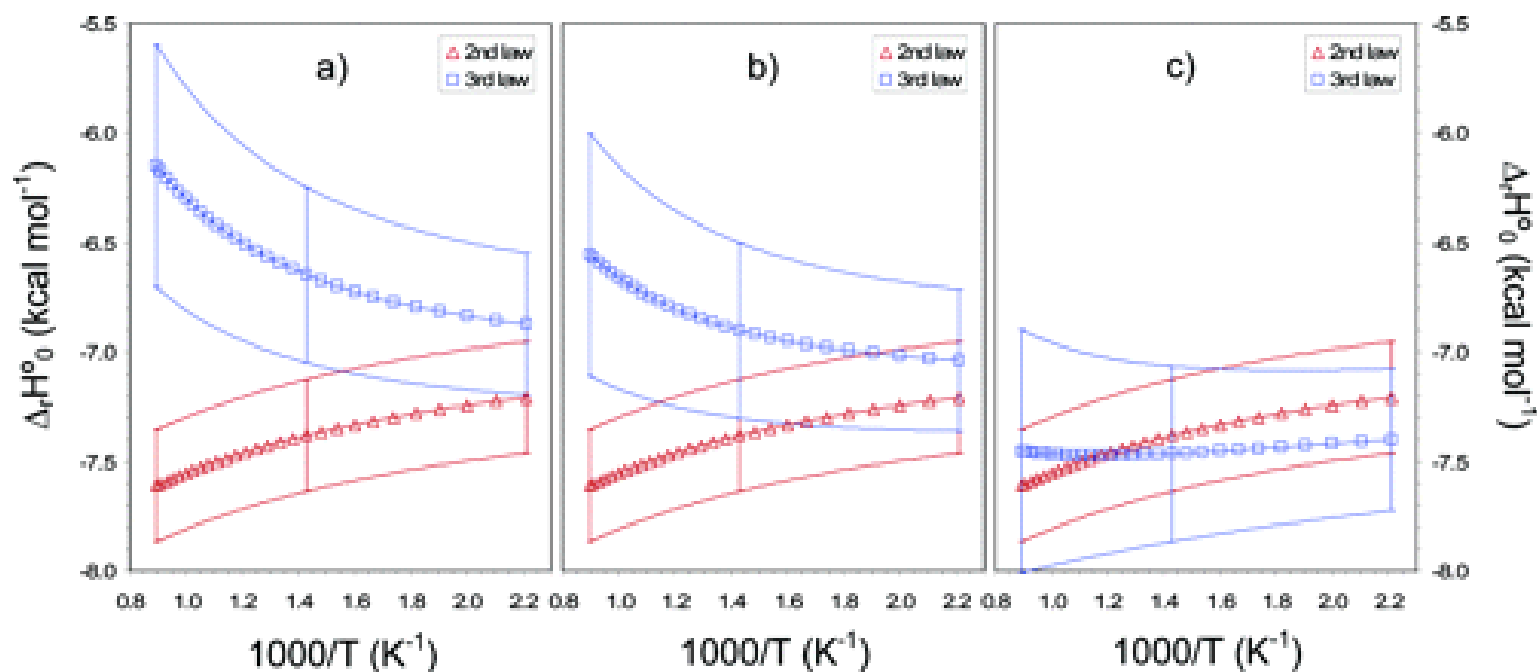
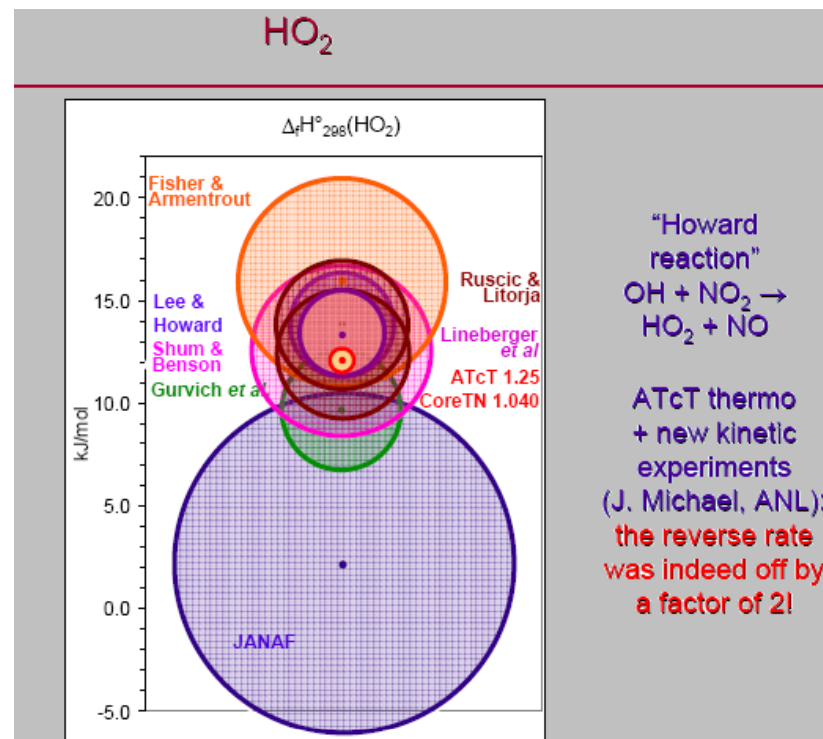
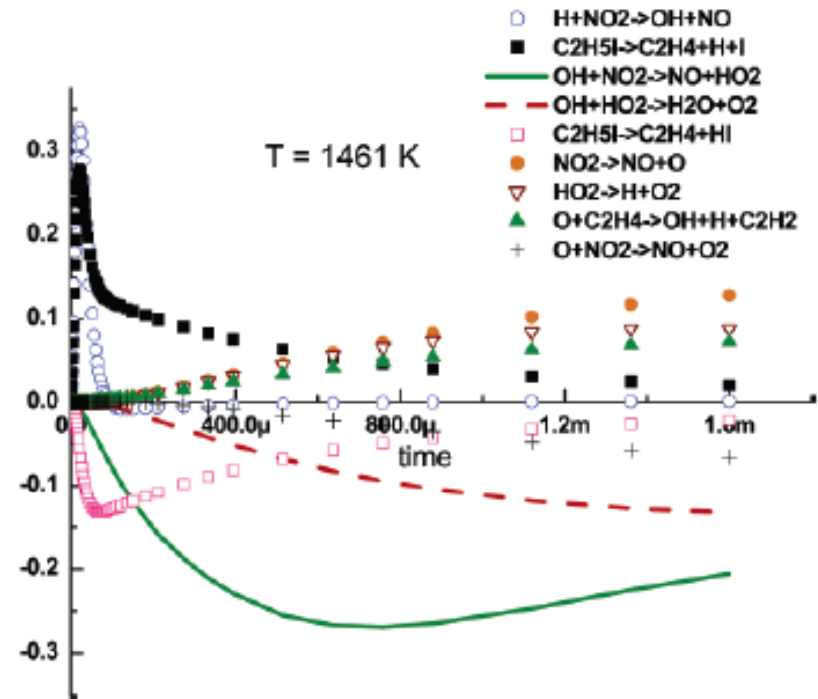
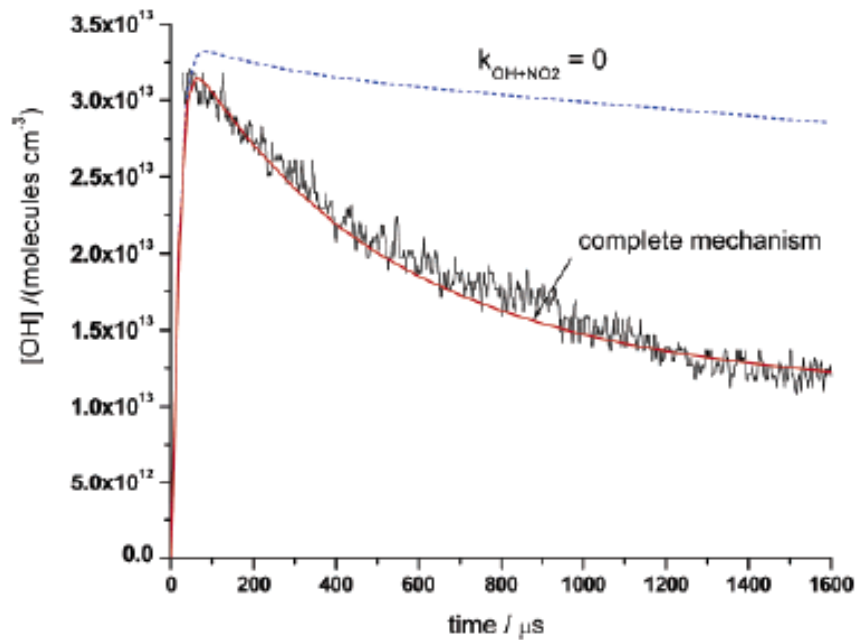


TABLE 1: Available Experimental Values for the Standard Enthalpy of Formation of HO₂ at 298 K (in kcal mol⁻¹)^a

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

Shock tube study of OH + NO₂

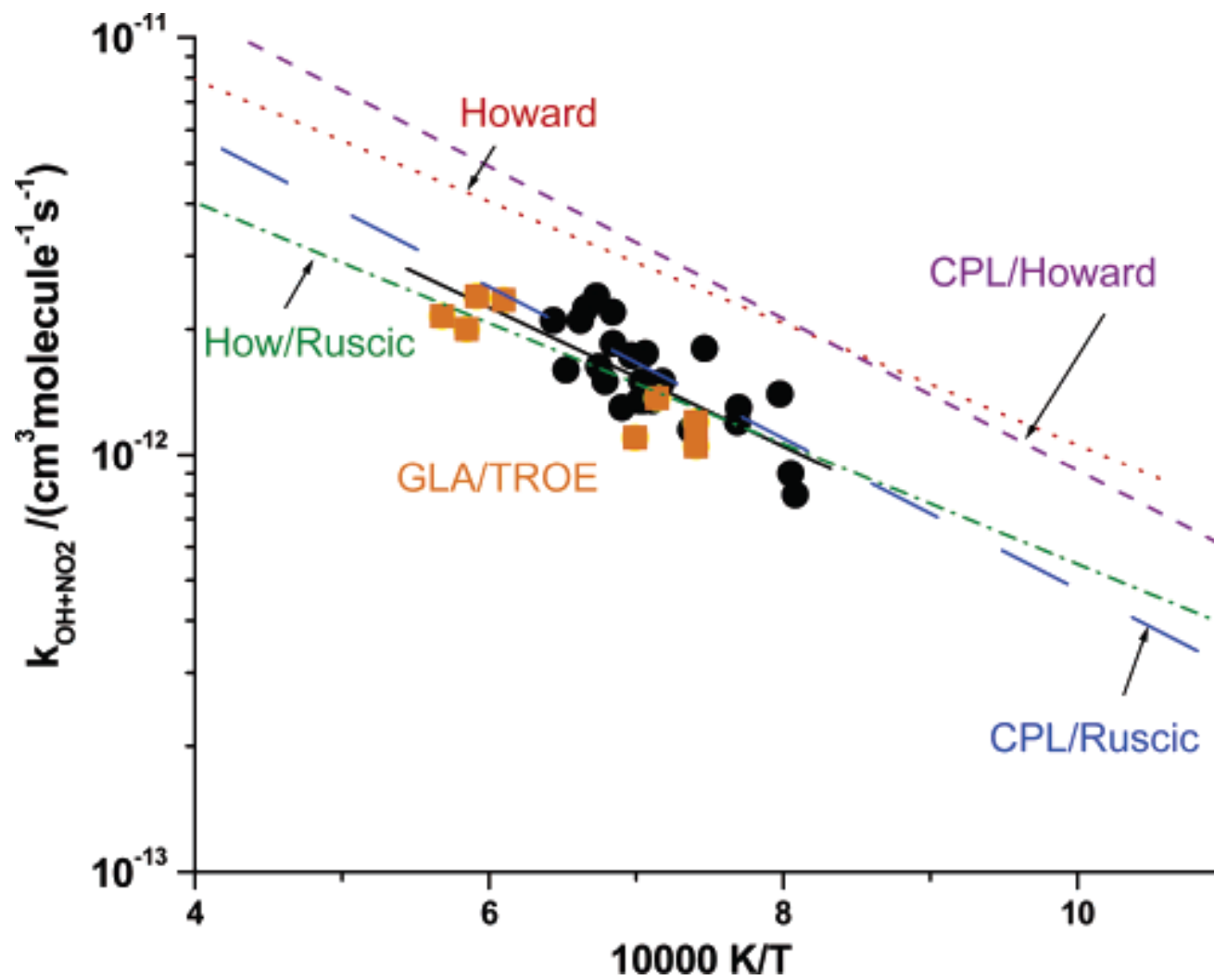
Srinivasan et al. *J. Phys. Chem. A* 2006, 110, 6602-6607



C₂H₅I + NO₂. OH from H + NO₂
1237 - 1554 K.

15 species, 23 sto mechanism, but sensitive to limited number of reactions

Comparison with Howard data



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

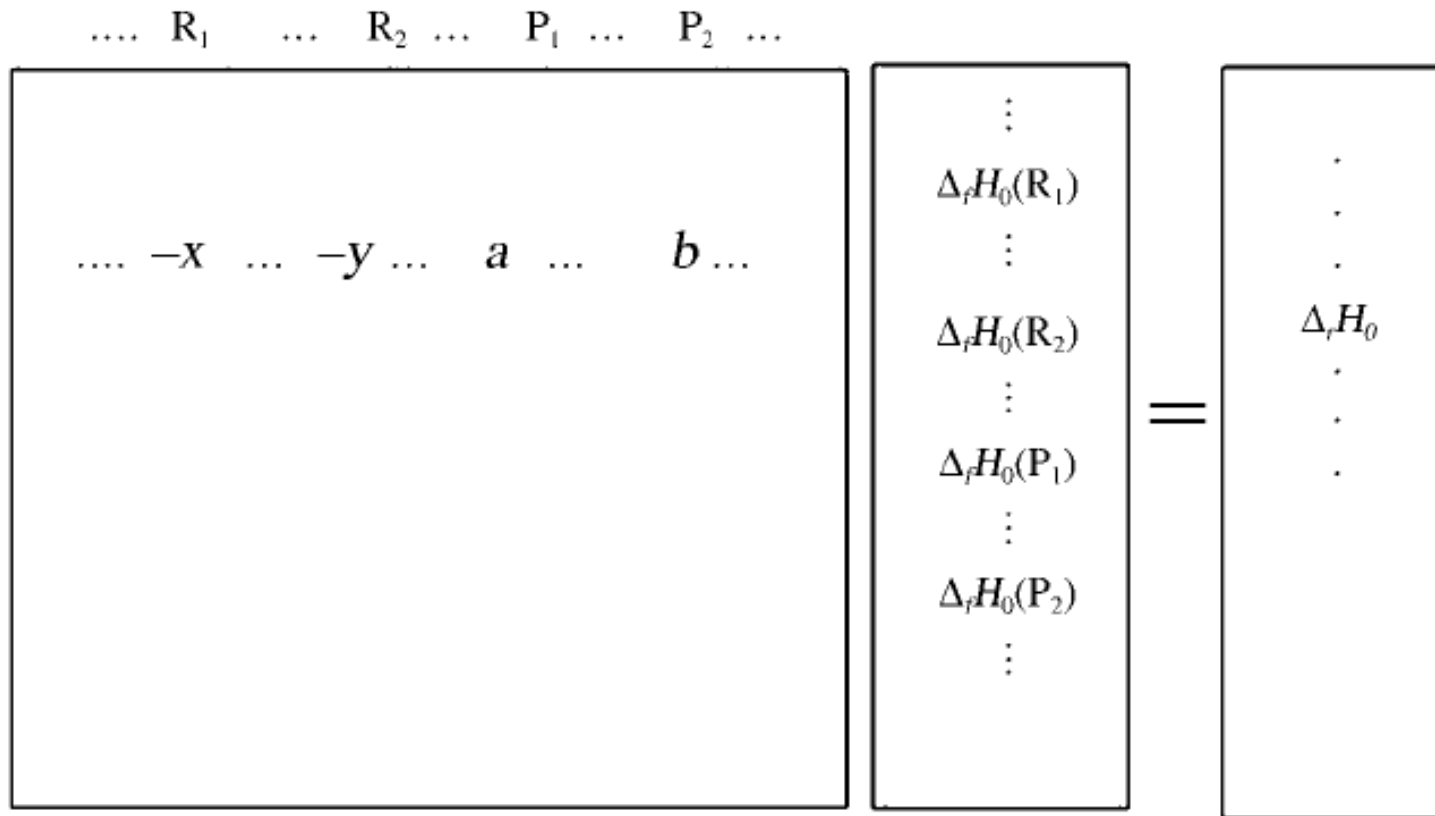


Figure 1. Pictorial representation of the NEAT protocol, which, after an inversion, leads to 0 K enthalpies of formation ($\Delta_f H_0$) from computed reaction enthalpies ($\Delta_r H_0$).

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 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