



# Chemical Kinetic Modelling for Combustion

Prof. Henry Curran

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# Overview/Aims

➤ 5 days / 15 lectures

➤ Day 1

➤ (1-3) Basic thermodynamic principles

➤ Day 2

➤ (4) Basic kinetic principles

➤ (5,6) Experimental JSR, FR, RCM & ST contribution to kinetics

➤ Day 3

➤ (7-9) Small species mechanism development



# Overview/Aims

➤ 5 days / 15 lectures

➤ Day 4

➤ (10-12) Large hydrocarbon mechanism development

➤ Day 5

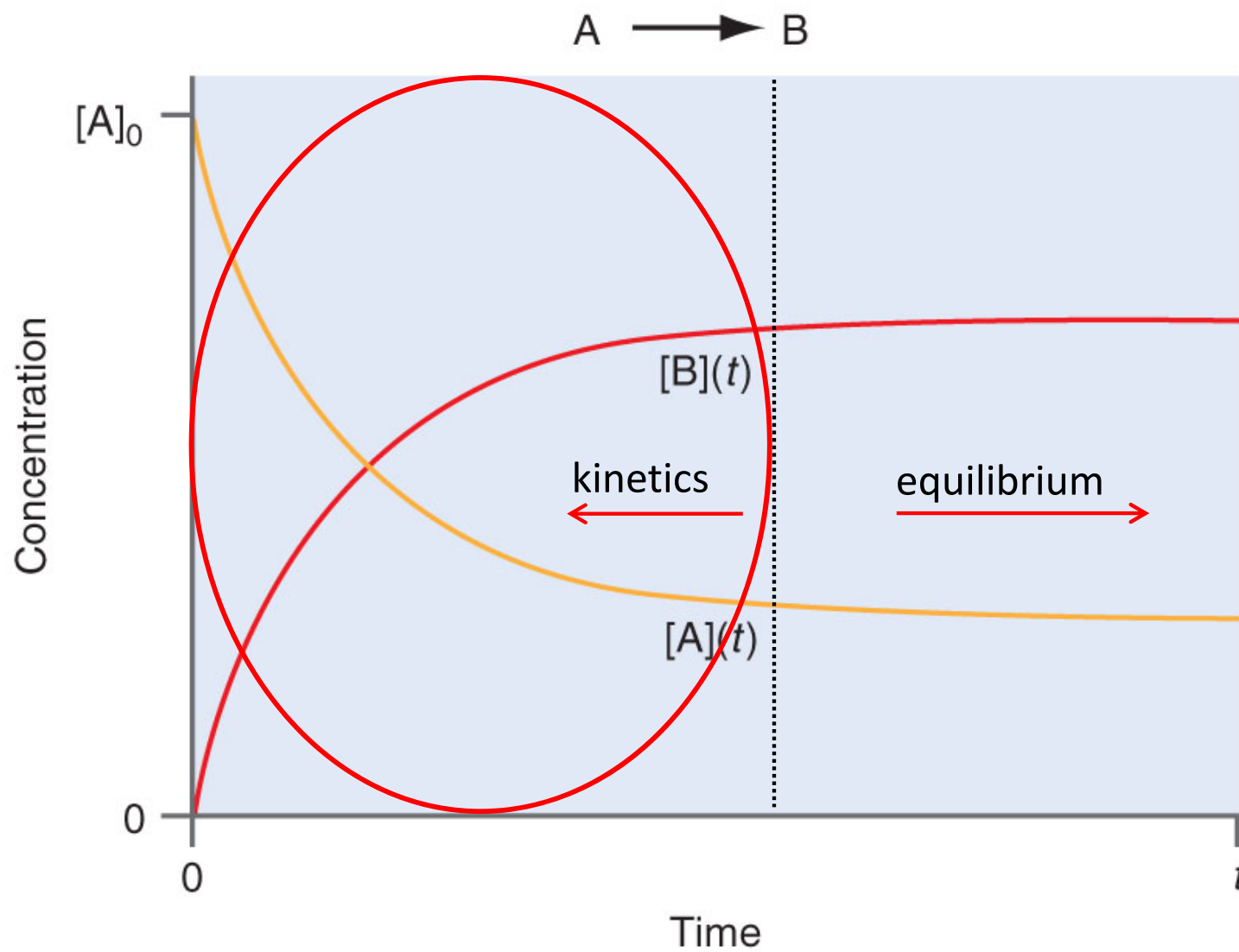
➤ (13-15) Oxygenated hydrocarbon mechanism development



# Basic kinetic and thermodynamic principles



# Kinetics and equilibrium



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# Thermodynamics

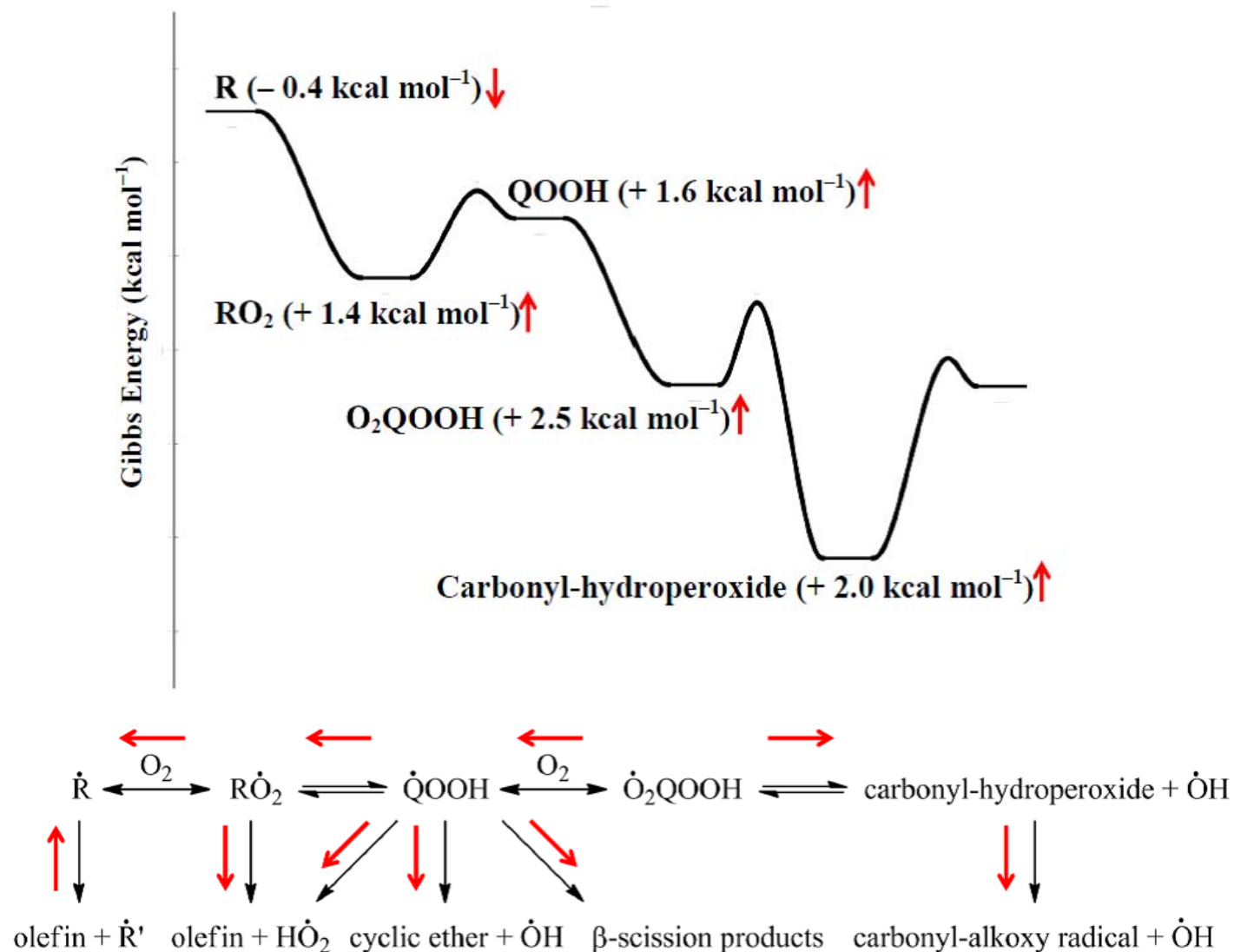
## Properties of interest:

- Entropy
- Enthalpy
- Heat capacity ( $C_p$  or  $C_v$ )
  - Can be used for extrapolation of above
- Gibbs free energy (follows from  $S$  and  $H$ )

## Why?

- Chemical equilibria ( $\ln K = -\Delta G/RT$ )
- Chemical insight/will a reaction happen?
  - endo vs. exothermic, spontaneous or not
- Heat release, adiabatic flame temp. etc.

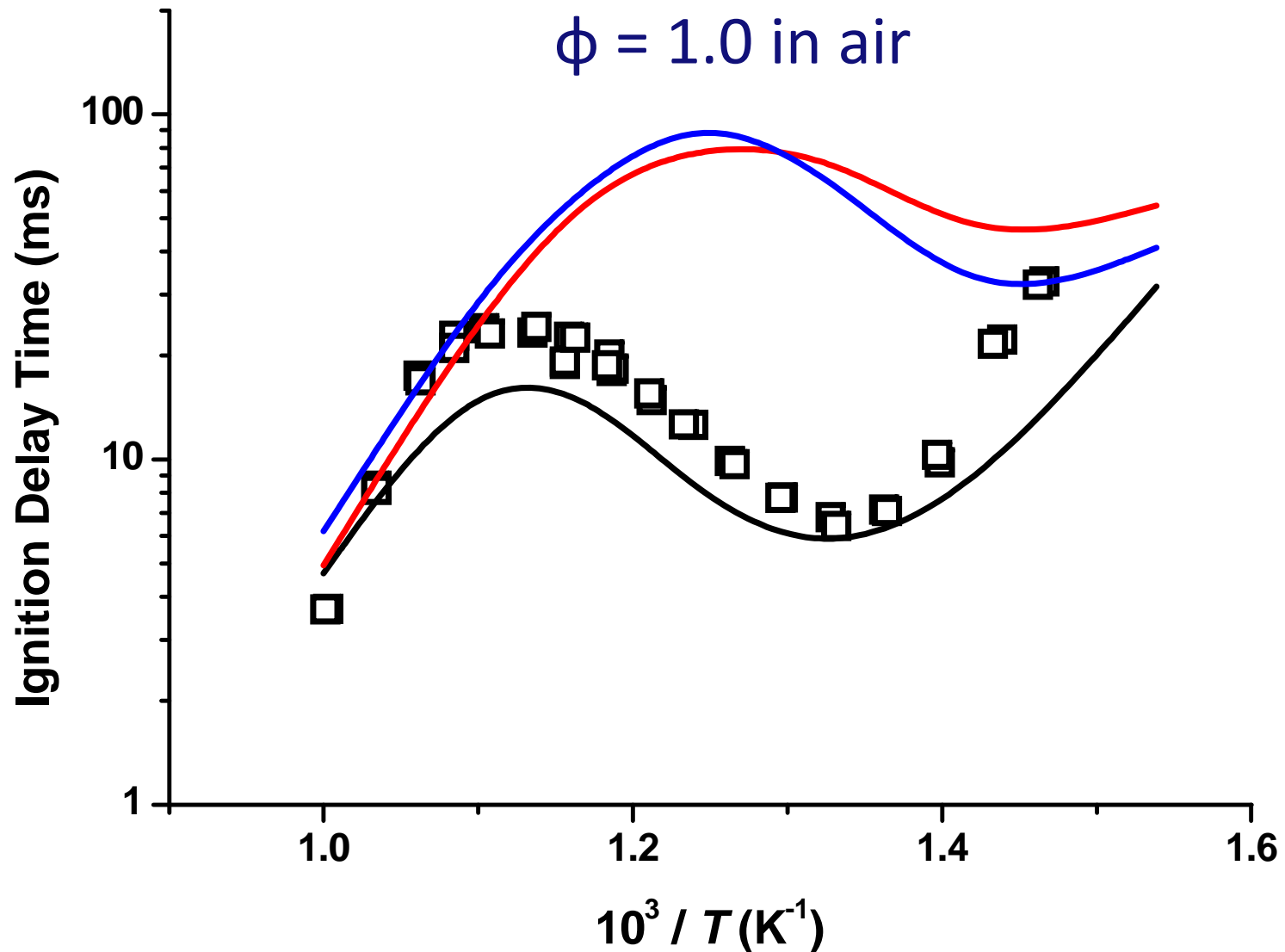
# Effect of thermochemistry on $\tau$



# Effect of thermochemistry on $\tau$

*n*-Pentane oxidation

$\phi = 1.0$  in air





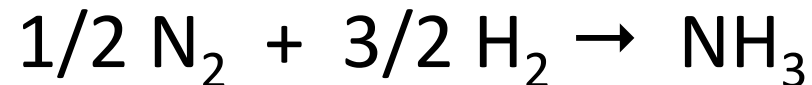


# Enthalpy of Formation

## Molar standard enthalpy of formation $\Delta_f H^\circ$ :

➤ Is the heat involved when one mole of a substance is produced from its elements in their standard state (1 bar for gases, usually 25°C).

➤ Standard enthalpy of formation of ammonia



➤ Conventionally, standard enthalpy of elements is fixed to 0 kJ/mol at standard state.

➤  $\text{H}_2$  for hydrogen gas,  $\text{O}_2$  for oxygen etc.

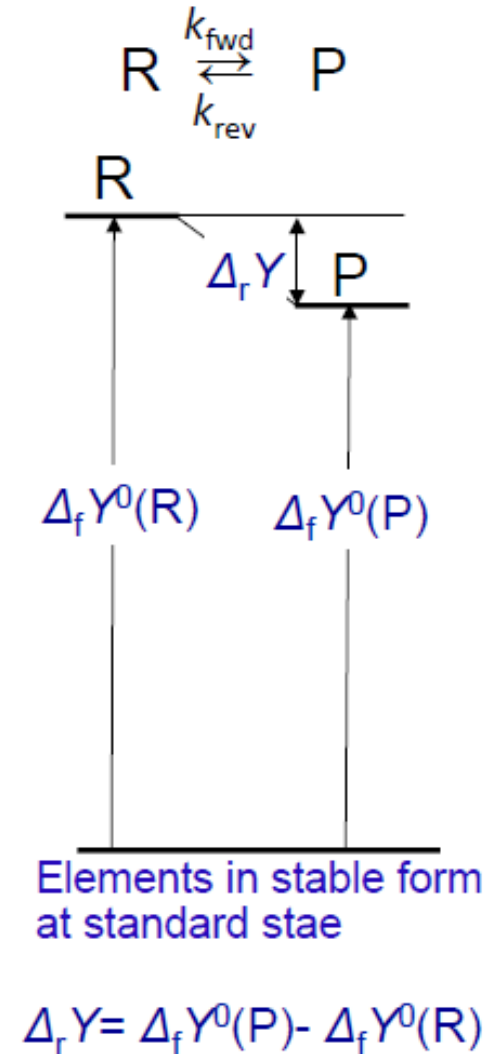
# Thermodynamic data

## Tabulated data

Standard enthalpy of formation,  $\Delta_f H^0$   
Standard entropy of formation,  $\Delta_f S^0$   
Specific heat capacity,  $C_p(T)$

## Sources of data

Experiments  
Ab initio calculations  
Empirical schemes based on  
observed rules in experimental or ab initio data



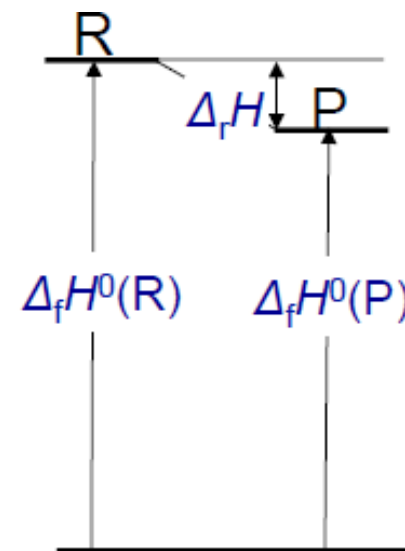
# Thermodynamic data: Experimental sources

## Enthalpy of formation, $\Delta_r H$

Determine the enthalpy change of any reaction  $\Delta_r H$

Calculate enthalpy of formation from  $\Delta_r H$   
and those of known reaction partners

$$\Delta_f H^0(R) = \Delta_r H + \Delta_f H^0(P)$$

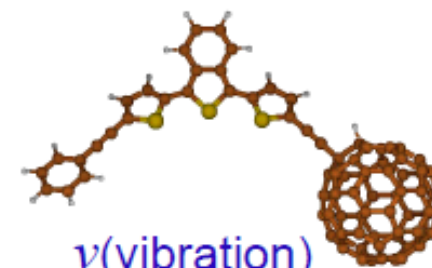


## Entropy of formation, $\Delta_r S$

Rarely measured directly

(from temperature dependence of  $K_r$ )

Calculated from experimental molecular parameters  
using statistical thermodynamics



$\nu$ (vibration)

$\Theta$ (inertia)

## Specific heat capacities, $C_p$

Can be measured directly for stable species

Calculated from experimental molecular parameters  
using statistical thermodynamic

generally simplified  
formulas of statistical  
thermodynamics

# Enthalpy of Formation

## Variation with temperature:

- At constant pressure:

$$\Delta H_{(T2-T1)} = Q_p = C_p \Delta T$$

- $C_p$  is the heat capacity at constant pressure of the compound.
- By integration, the enthalpy of formation of a compound at a temperature  $T$  is calculated by:

$$\Delta_f H^\circ_{(T)} = \Delta_f H^\circ_{298\text{K}} + \int_{298}^T \Delta_r C_P^\circ dT = \Delta_f H^\circ_{298\text{K}} + \int_{298}^T (C_{P_{\text{molecule}}}^\circ - C_{P_{\text{elements}}}^\circ) dT$$

- Permits derivation an analytic expression as a function of  $T$



# Entropy

- Linked to the number of states of the particles in the system
- In a reversible transformation  $\Delta_r S = Q/T$
- The entropy represents the extensivity of the thermal energy of a system at the temperature T.
- Entropy of elements at 0 K = 0 kJ/mol
- **Free Energy** (Gibbs, G) indicates spontaneity of reaction
  - Dependent on Enthalpy and Entropy
  - Contribution of Entropy becomes important as T increases

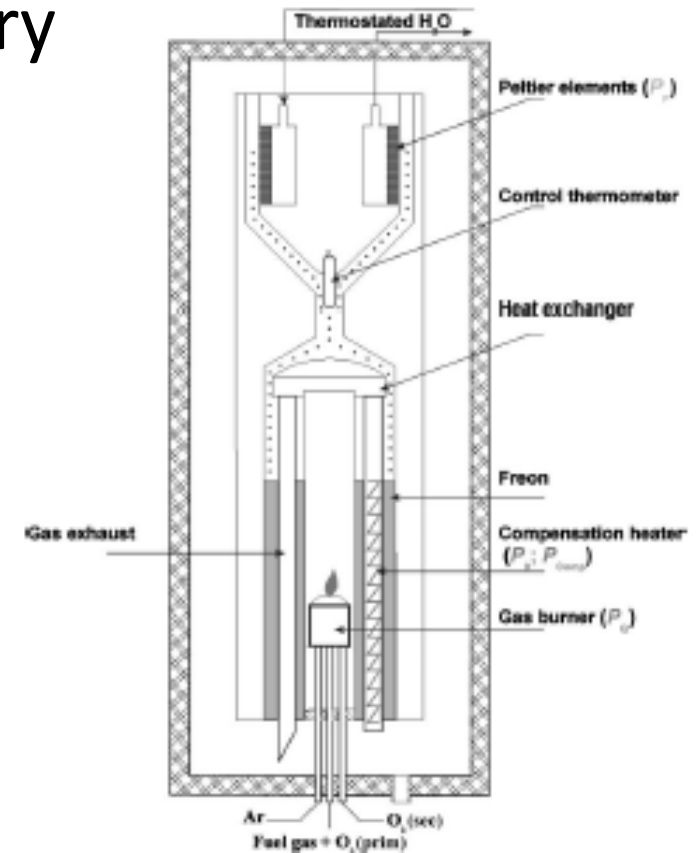
$$G = H - TS$$

# Thermodynamics

## How do we determine $C_p$ , $S$ , $H$ ?

- Experiment—Combustion Calorimetry
  - Foundation of thermodynamics BUT....
  - Time consuming
  - Difficult/expensive
  - Fine for stable species, what about radicals?

Modern design



Y.I. Alexandrov *Thermochim. Acta* **382**, 55



# Non-experimental methods

## Ab initio quantum chemistry

Solving the Schrödinger equation for a molecule provides its energy and its thermodynamic properties

In principle.

In fact, the methods of ab initio quantum chemistry are approximate

## Estimation of thermodynamic parameters based on empirical rules

Group additivity method

## Ab initio methods

are based on a few approximations

and a real effort to fix the problems of the approximations

## Group additivity

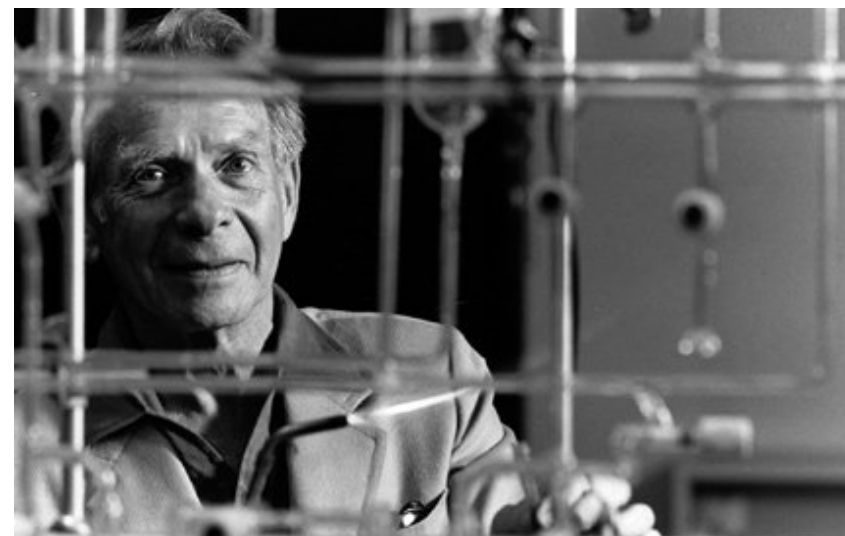
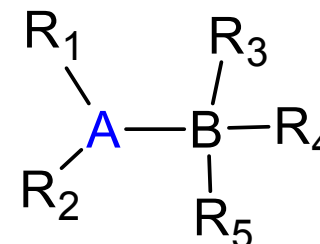
within certain limits of accuracy the thermodynamic properties of properly selected groups add up to that of a molecule

data can be borrowed from information on one or more similar molecules  
the question is the “limit of accuracy”.

# Group Additivity

## What is it?

- Empirical method for estimation of thermodynamics
- Pioneered by Prof. Sidney W. Benson
- Thermodynamic functions dependent on:
  - Nature of each atom in a molecule and
  - Nature of each of their bonding partners (short range effects)
  - Long range effects can be important
- Molecule split into groups
- Each group makes a contribution to thermo. functions of molecule







# Group Additivity

## Consider Ethane:

- Simple molecule with **2 identical groups** (C/C/H<sub>3</sub>)



- Thermodynamics well known
- $\Delta H_f^0 = -84. \pm 0.4 \text{ kJ/mol}$  (NIST)
  - Contribution of each group = -42.0 kJ/mol
- $C_p$  298.15 K = 52.49 J/mol (NIST)
  - Contribution of each group = 26.25 J/mol
- $S^0$  298.15 K = 229.28 J/mol
  - Contribution of each group.....not as simple
  - Corrections for molecular symmetry are applied

# Group Additivity

## Entropy calculations:

➤ Sum of the group contributions: intrinsic entropy  $S^\circ_i$

➤ Correction for symmetry:

$$\delta S^\circ = -R \ln \sigma$$

➤  $\sigma$  = number of symmetries in the molecule =  $\sigma_{\text{ext}} \times \sigma_{\text{int}}$

–  $\sigma_{\text{ext}}$  number of external symmetries (rotation of molecule)

–  $\sigma_{\text{int}}$  number of internal symmetries (rotations around single bonds)

➤ Ethane  $\sigma_{\text{ext}} = 2$ ,  $\sigma_{\text{int}} = 9$ , total correction =  $-R \ln(18)$

➤ Similar corrections for optical isomers =  $+R \ln(\# \text{ of OI})$

# Group Additivity

## What about free radicals?

- Estimated through definition of 'Bond Increments' or 'Bond Dissociation' values for H, S and C<sub>p</sub>
- $\text{RH} \rightarrow \text{R}\cdot + \text{H}\cdot$   $\Delta_r H = \text{Bond Dissociation Energy (BDE)}$

- $\Delta H_f^0(\text{R}\cdot) = \text{BDE} + \Delta H_f^0(\text{RH}) - \Delta H_f^0(\text{H}\cdot)$

Varies based on  
type of C-H bond  
broken

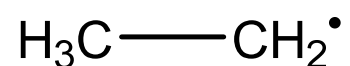
Heat of  
formation  
of 'parent'  
species

Well known  
 $\Delta_f H = 52.1$   
kcal/mol

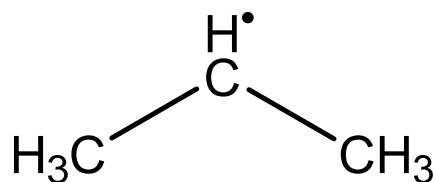
# Group Additivity

## BDE Groups

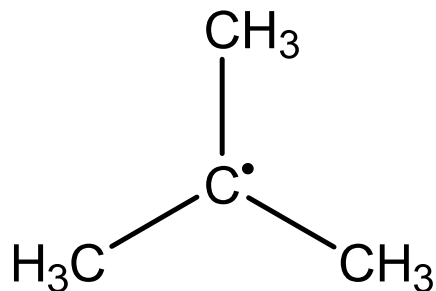
- Strength of C–H bond depends on stability of radical



Type = primary, 101.1 kcal/mol



Type = secondary, 98.45 kcal/mol

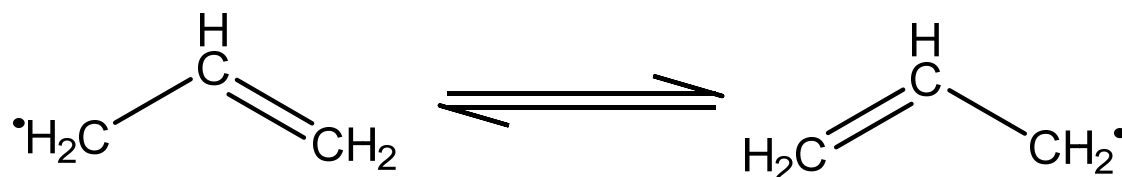


Type = tertiary, 96.50 kcal/mol

# Group Additivity

## BDE Groups

- Strength of C–H bond depends on stability of radical
- Electron delocalization leads to more stable radicals
  - Reduces BDE



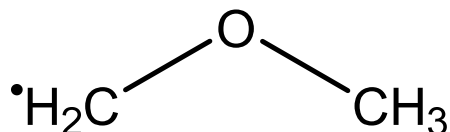
Type = primary allylic, 88.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)

# Group Additivity

## BDE Groups

- Locally bonded electronegative atoms reduce BDE



96.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)



# Group Additivity

## Can be applied to:

- Alkanes, alkenes, alkynes
- Alcohols, ethers
- Ketones, aldehydes
- Cycloalkanes, aromatics
- Pretty much everything...BUT...
- Parameterization against experiment and/or quantum chemical calculations necessary for best results and widest range of applicability



# Groups and super-atoms

Atom differentiation according to the type of liaison

$C$ :  $sp^3$  carbon atom, 4 single bonds

$C_d$ :  $sp^2$  carbon atom, 1 double bond, 2 single,  $\equiv$  divalent atom

$C_t$ :  $sp$  carbon atom, 1 triple bond, 1 single,  $\equiv$  monovalent atom

$C_a$ : allene-like carbon atom,  $C=C=C$ , ending atoms are  $C_d$

$C_B$ : carbon-atom in aromatic rings,  $\equiv$  trivalent atom

$C_{BF}$ : “fused carbon” carbon-atom belonging to several aromatic rings,  $\equiv$  trivalent atom

Super-atoms:

$C=O$ , carbonyl group  $\equiv$   $(CO)$  divalent

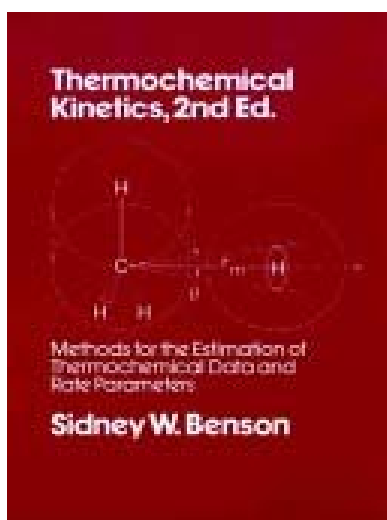
$NO$ ,  $NO_2$ ,  $SO_2$ ,  $PO$ ...



# Benson's groups

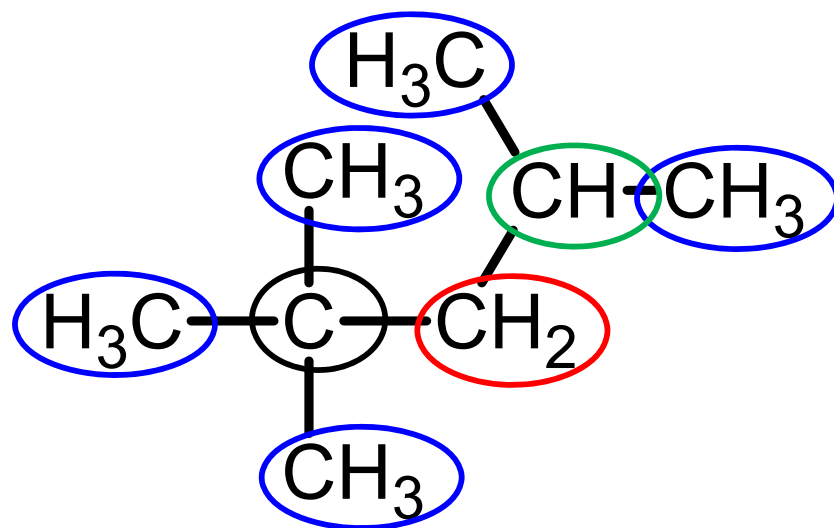
**Table A.1. Group Values for  $\Delta H_f^\circ$ ,  $S_{int}^\circ$ , and  $C_p^\circ$  Hydrocarbons**

Group	$\Delta H_f^\circ$ 298	$S_{int}^\circ$ 298	$C_p^\circ$					
			300	400	500	600	800	1000
C—(H) <sub>3</sub> (C)	-10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77
C—(H) <sub>2</sub> (C) <sub>2</sub>	-4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34
C—(H)(C) <sub>3</sub>	-1.90	-12.07	4.54	6.00	7.17	8.05	9.31	10.05
C—(C) <sub>4</sub>	0.50	-35.10	4.37	6.13	7.36	8.12	8.77	8.76
C <sub>d</sub> —(H) <sub>2</sub>	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27
C <sub>d</sub> —(H)(C)	8.59	7.97	4.16	5.03	5.81	6.50	7.65	8.45
C <sub>d</sub> —(C) <sub>2</sub>	10.34	-12.70	4.10	4.61	4.99	5.26	5.80	6.08
C <sub>d</sub> —(C <sub>d</sub> )(H)	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
C <sub>d</sub> —(C <sub>d</sub> )(C)	8.88	-14.6	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)
[C <sub>d</sub> —(C <sub>B</sub> )(H)]	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
C <sub>d</sub> —(C <sub>B</sub> )(C)	8.64	(-14.6)	(4.40)	(5.37)	(5.93)	(6.18)	(6.50)	(6.62)
[C <sub>d</sub> —(C <sub>t</sub> )(H)]	6.78	6.38	4.46	5.79	6.75	7.42	8.35	8.99
C <sub>d</sub> —(C <sub>B</sub> ) <sub>2</sub>	8.0							
C <sub>d</sub> —(C <sub>d</sub> ) <sub>2</sub>	4.6							



# Group Additivity

## 2,2,4-trimethylpentane (iso-octane):



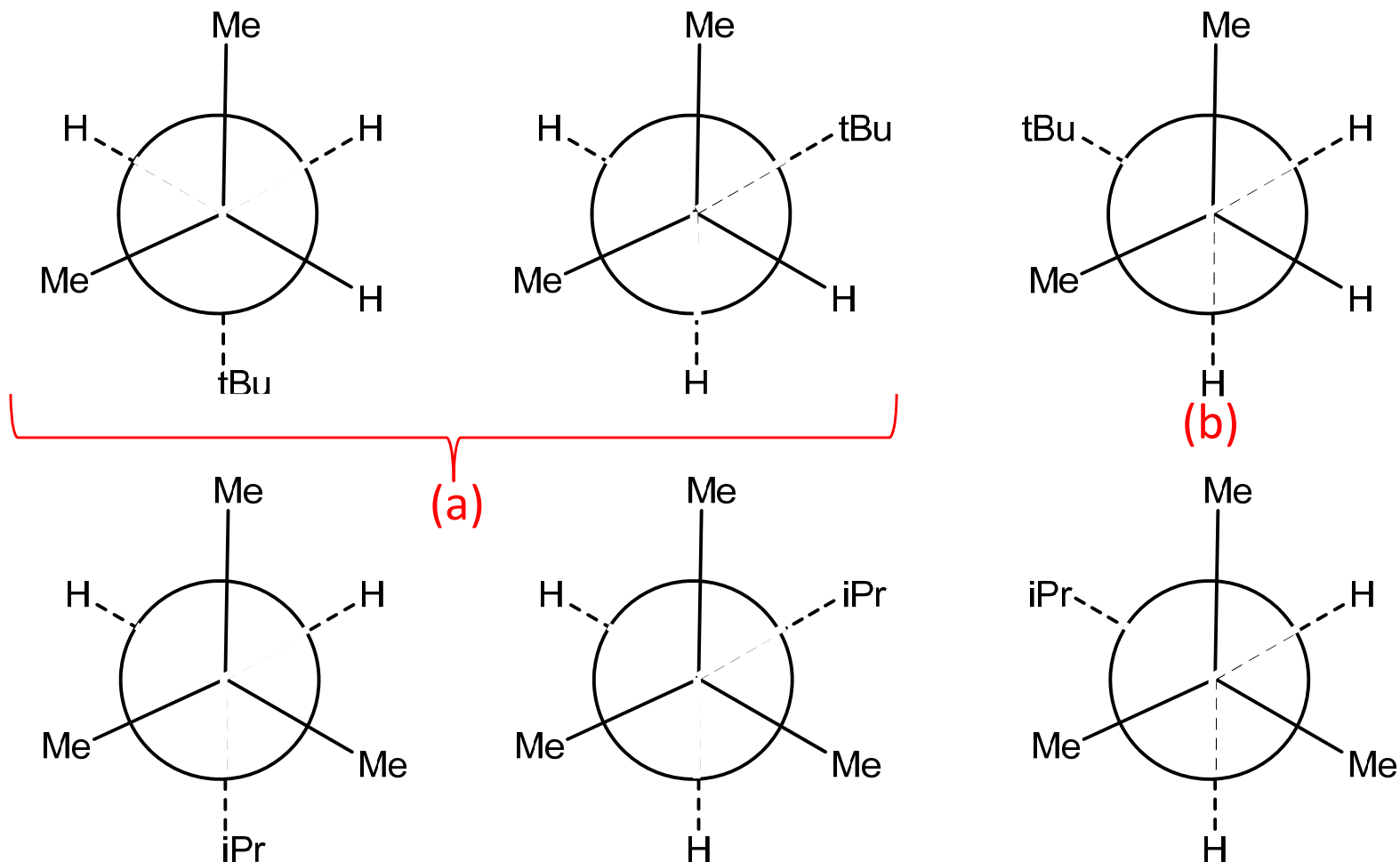
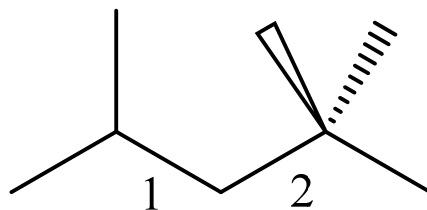
C-(H) <sub>3</sub> (C)	5 groups
C-(H) <sub>2</sub> (C) <sub>2</sub>	1 group
C-(H)(C) <sub>3</sub>	1 group
C-(C) <sub>4</sub>	1 group

$$\sigma_{\text{ext}} = 1, \sigma_{\text{int}} = 729$$

Correction to symmetry

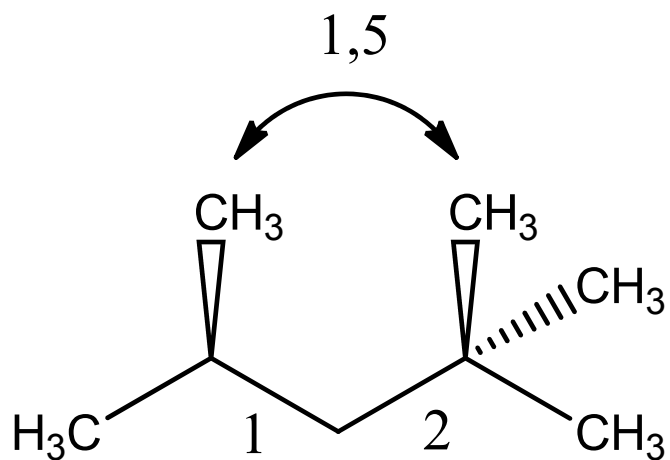
$$-R \ln(729) = -13.1 \text{ cal/mol/K}$$

# Gauche (C–C) interactions

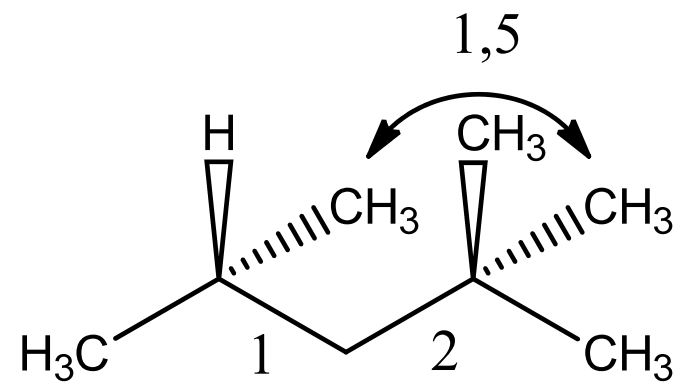




# 1,5 (H-H) Interaction



or



1.5 kcal/mol



# Group additivity in action

## 2,2,4-trimethylpentane (iso-octane):

group	number	$\Delta H^\circ$ (298K) kcal/mol	$S^\circ$ (298K) cal/mol/K	$C_p^\circ$ (300 K) cal/mol/K
C/C/H <sub>3</sub>	5	-10.03	30.42	6.26
C/C2/H2	1	-4.960	9.42	5.44
C/C3/H	1	-2.130	-12.02	4.39
C/C4	1	0.100	-34.99	4.01
gauche	3	0.7	0	0
H/REPEL/15	1	1.5	0	0
symmetry			-R ln729	
total		-53.54	101.41	45.14

# Software

## Benson's Additivity Method

**THERM** Ritter and Bozzelli Int. J. Chem. Kinet. 23 (1991) 767-778.

Decomposition into groups and corrections done by the user

**NIST database program** Stein et al. (1991) Webbook

(<http://webbook.nist.gov/chemistry/grp-add/>)

**THERGAS** C. Muller, V. Michel, G. Scacchi and G. M. Côme, J. Chem. Phys. 92 (1995) 1154-1177.

**CRANIUM** : groups of Joback, estimation of other properties

( $T_{eb}$ ,  $T_{fus}$ ,  $T_c$ ,  $P_c$ ...)

(<http://www.molknow.com/Online/Estimation.htm>)

## Quantum Chemistry softwares

Semi-empirical approach: MOPAC...

Ab initio : Gaussian, Spartan, Jaguar, Molpro, ...

# Thermochemistry in Chemkin

Chemkin uses standard state thermodynamic properties given as polynomial fits to the specific heats at constant  $p$

$$\frac{C_p^o k}{R} = \sum_{n=1}^N a_{nk} T^{(n-1)}$$

$$H_k^o = \int_0^T C_p^o k dT$$

$$\frac{H_k^o}{RT} = \sum_{n=1}^N \frac{a_{nk} T^{(n-1)}}{n} + \frac{a_{N+1,k}}{T}$$

where  $a_{N+1,k}R$  is the standard heat of formation at 0 K, but is normally evaluated from the heat of formation at 298 K.



# Thermochemistry in Chemkin

$$S_k^o = \int_0^T \frac{C_{p^k}^o}{T} dT$$
$$\frac{S_k^o}{R} = a_{1k} \ln T + \sum_{n=2}^N \frac{a_{nk} T^{(n-1)}}{(n-1)} + a_{N+2,k}$$

where  $a_{N+2,k}R$  is evaluated from knowledge of the standard-state entropy at 298 K.

These are stated for arbitrary-order polynomials, but Chemkin is designed to use NASA polynomials. In this case seven coefficients are needed for each of two temperature ranges. These fits follow the form:





# Thermochemistry in Chemkin

$$\frac{C_p^o k}{R} = \sum_{n=1}^N a_{nk} T^{(n-1)}$$

$$\frac{C_p^o k}{R} = a_{1k} + a_{2k} T + a_{3k} T^2 + a_{4k} T^3 + a_{5k} T^4$$

$$\frac{H_k^o}{R} = \int_0^T \frac{C_p^o k}{R} dT = a_{1k} T + \frac{a_{2k}}{2} T^2 + \frac{a_{3k}}{3} T^3 + \frac{a_{4k}}{4} T^4 + \frac{a_{5k}}{5} T^5 + a_{6k}$$

$$\frac{H_k^o}{RT} = a_{1k} + \frac{a_{2k}}{2} T + \frac{a_{3k}}{3} T^2 + \frac{a_{4k}}{4} T^3 + \frac{a_{5k}}{5} T^4 + \frac{a_{6k}}{T}$$

Other thermodynamics properties are easily given in terms of  $C_p^o$ ,  $H^o$ , and  $S^o$



# Thermochemistry in Chemkin

$$\frac{C_p^o k}{R} = \sum_{n=1}^N a_{nk} T^{(n-1)}$$

$$\frac{C_p^o k}{R} = a_{1k} + a_{2k}T + a_{3k}T^2 + a_{4k}T^3 + a_{5k}T^4$$

$$\frac{S_k^o}{R} = \int_0^T \frac{C_p^o k}{RT} dT = a_{1k} \ln T + a_{2k}T + \frac{a_{3k}}{2}T^2 + \frac{a_{4k}}{3}T^3 + \frac{a_{5k}}{4}T^4 + a_{7k}$$

Other thermodynamics properties are easily given in terms of  $C_p^o$ ,  $H^o$ , and  $S^o$

# NASA polynomials

THERMO

300., 1000., 5000.

```

C6H5O      3/20/89 THERMC   6H   50   1   OG   300.000  5000.000  1404.000   01
1.57324764E+01 1.54394760E-02-5.31383756E-06 8.28591116E-10-4.82238305E-14   2
-1.76799222E+03-6.20052317E+01-3.73072513E+00 6.71840729E-02-5.88121307E-05   3
2.61335718E-08-4.61968583E-12 4.31827564E+03 4.02213334E+01   4
CH3OCH3    3/20/89 THERMC   2H   60   1   OG   300.000  5000.000  1364.000   21
8.43631162E+00 1.30235626E-02-4.45885307E-06 6.93233262E-10-4.02757540E-14   2
-2.62777965E+04-2.24530764E+01 1.53263200E+00 2.37669572E-02-8.14177550E-06   3
-5.29451929E-10 5.96605679E-13-2.32831259E+04 1.66340885E+01   4
END
  
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column numbers:

1	10	20	30	40	50	60	70	80
23456789	123456789	123456789	123456789	123456789	123456789	123456789	123456789	123456789
<-name>	<-date->	<ref>	<---- elements ---->	G	<- Tlow >	<- Thi->	<- Tbk->	21
<---- a1 ---->	<---- a2 ---->	<---- a3 ---->	<---- a4 ---->	<---- a5 ---->	<---- a6 ---->	<---- a7 ---->	<---- a8 ---->	2
<---- a6 ---->	<---- a7 ---->	<---- a8 ---->	<---- a9 ---->	<---- a10 ---->	<---- a11 ---->	<---- a12 ---->	<---- a13 ---->	3
<---- a11 ---->	<---- a12 ---->	<---- a13 ---->	<---- a14 ---->	<---- a15 ---->	<---- a16 ---->	<---- a17 ---->	<---- a18 ---->	4

E.R. Ritter J.W. Bozzelli  
*Intl. J. Chem. Kinet.*, 23 (1991) 767-778.



# Thermochemical databases

**JANAF Thermochemical Tables** 3rd ed., vols. 1-2 , M.W. Chase, American Chemical Society, 1986, SELREF/QD516.D695 1986

Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds: Chapman & Hall, London, 1986.

Tables **TRC** (Thermodynamics Research Center) Thermodynamic Tables - Hydrocarbons - Department of Chemistry, Texas A&M University

## Online databases:

NIST Webbook : <http://webbook.nist.gov/>

Computational Chemistry Comparison and Benchmark Data Base  
<http://webbook.nist.gov/chemistry/>

Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion (Burcat) : [http://www.dlr.de/vt/en/desktopdefault.aspx/tabid-7603/12862\\_read-32379/](http://www.dlr.de/vt/en/desktopdefault.aspx/tabid-7603/12862_read-32379/)

Active Thermochemical Tables (Branco Ruscic Argonne National Lab.)  
<https://atct.anl.gov/Thermochemical%20Data/version%201.122/index.php>