Topic 5
Evaluation of rate data

Examination of available rate data from the literature and recommendation of rate parameters over specified temperature range, together with uncertainties.

Compatibility with experimental global observables

Evaluated Kinetic Data for Combustion Modeling: Supplement II

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The next few slides show the structure of a typical data sheet

Example $O + OH \rightarrow O_2 + H$

1. Thermodynamic Data

ΔH°_{298} = -68.29 kJ mol^{-1}

ΔS°_{298} = -25.04 J K^{-1} mol^{-1}

K_c = 3.48·10^{-3} $T^{0.367}$ exp(+8390/ T)

$(300 \leq T/K \leq 5000)$

2. Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{-11} \exp(112/T)$	221—499	Lewis and Watson, 1980[1]	(a)
$3.8 \cdot 10^{-11}$	258	Howard and Smith, 1980[2]	(b)
$6.7 \cdot 10^{-10} T^{-0.5}$	250—515	Howard and Smith, 1981[3]	(b)
$3.1 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson, 1983[4]	(c)
$3.5 \cdot 10^{-11}$	299	Keyser, 1983[5]	(d)
$4.2 \cdot 10^{-11}$	294	Smith and Stewart, 1994[6]	(e)
$4.5 \cdot 10^{-11}$	227		
$5.2 \cdot 10^{-11}$	190		
$6.1 \cdot 10^{-11}$	158		
Reviews and Evaluations			
$5.42 \cdot 10^{-13} T^{0.375} \exp(1112/T)$	1000—5300	Michael, 1992[7]	(f)
$2.0 \cdot 10^{-11} \exp(112/T)$	220—500	CEC, 1992; 1994[8]	(g)
$2.4 \cdot 10^{-11}$	1000—2000		
$2.2 \cdot 10^{-11} \exp(120/T)$	220—500	NASA, 1997[9]	(h)
$2.3 \cdot 10^{-11} \exp(110/T)$	220—500	IUPAC, 1997[10]	(i)

Provides data on recent measurements and evaluations, including
Rate coefficient
T/K
Reference
Link to comments

Comments (examples)

(e) Fast flow system in which OH radicals were created by pulsed laser photolysis at 266 nm of HNO_3 in the presence of a much higher concentration of O atoms previously produced upstream of the HNO_3 injection point by the N+NO reaction. [OH] was monitored by LIF, pumping at ~ 282.5 nm and observing at ~ 310 nm. The time delay between the pulse generating OH and the LIF probe pulse was varied. Results were also obtained at 103 K, 50 K, and 10 K but with large uncertainties.

(f) Calculated from thermodynamic data and $k(H+O_2)$.

(g) Expression of Lewis and Watson[1] adopted for low temperature range and high temperature expression derived from thermodynamic data and $k(H+O_2)$.

Preferred values

- $k = 2.00 \cdot 10^{-10} \ T^{-0.352} \exp(113/T) \ cm^3 \ molecule^{-1} \ s^{-1}$ over the range 250-3000 K.

- *Reliability*
- $\Delta\log k = \pm 0.2$ over the range 250-3000 K.

Comments on preferred values

- The only direct studies on this reaction have been carried out at low temperatures where there is excellent agreement among the more recent of them.

- Although there have been no direct measurements of k above 515 K the reverse reaction has been extensively investigated at temperatures in the range 800-3400 K. The preferred expression for k has been derived, therefore, by a fit to the data obtained by combining the expression for $k(H+O_2)$ from the present evaluation with the thermodynamic data at temperatures above 800 K together with the directly obtained experimental data at temperatures below 500 K. The reaction has been the subject of a number of theoretical studies; see Miller,[19-21] Troe,[22] Harding *et al.*[23] and Troe and Ushakov.[24]

Arrhenius Plot
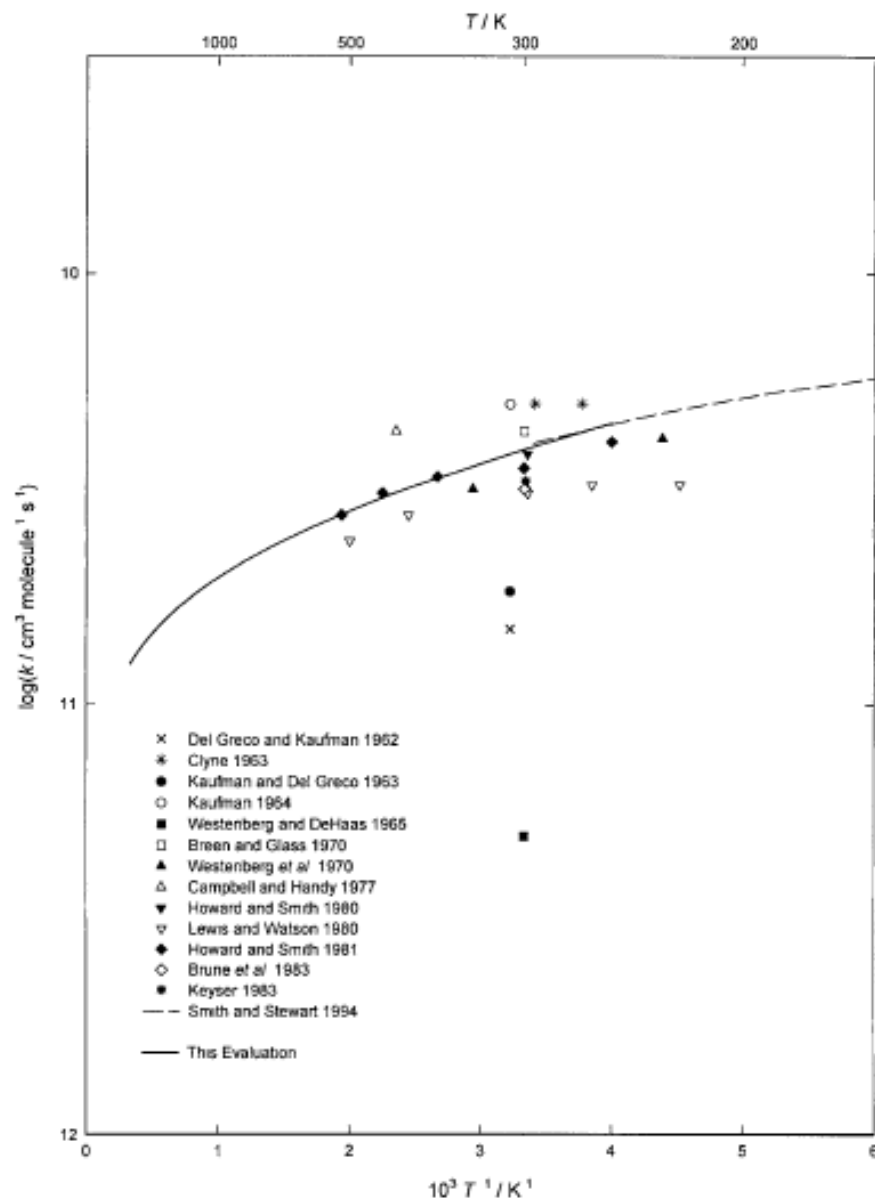
Reverse reaction: $H + O_2 \rightarrow O + OH$

- $k = 3.43 \cdot 10^{-10}\ T^{-0.097}\ \exp(-7560/T)$ cm^3 molecule^{-1} s^{-1} over the range 800-3500 K.
- $\Delta \log k = \pm 0.1$ at 800 K, rising to ± 0.2 at 3500 K.
- There are no direct measurements of k below 500 K and the recommended values are based on data obtained at temperatures above 800 K. The majority of the determinations of k have been made using shock tube techniques and, generally, are in good agreement.[1-10,15-25] There is a trend in the more recent studies[1-10] to give slightly lower values of E/R than most of the older determinations.[11,5-25] Our preferred expression for k is based on the more recent studies, which are cited in the Table. The expression derived gives values very similar to the expression used by Smith *et al.*[26] in modelling studies using the GRI mechanism.
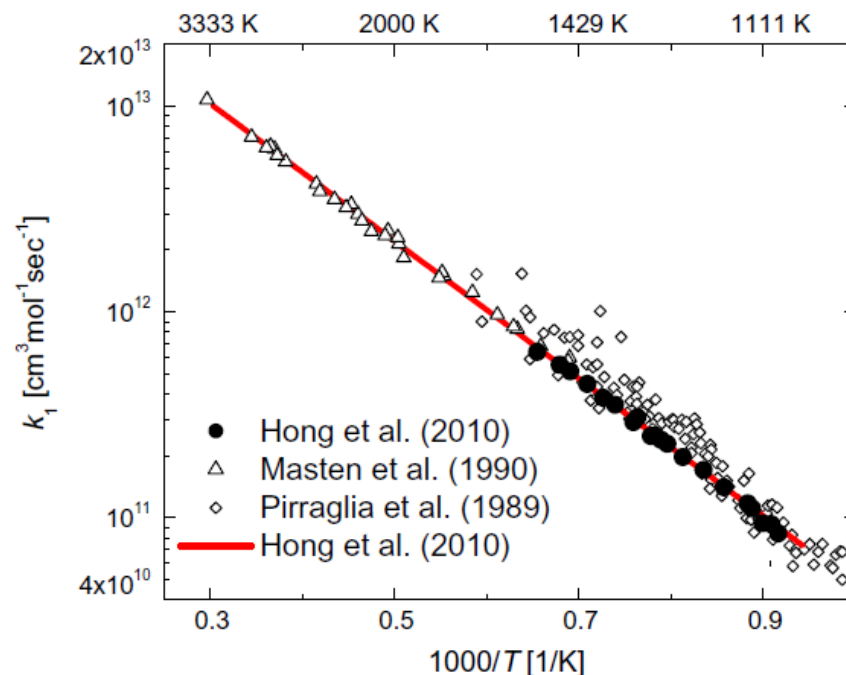
$H + O_2 \rightarrow O + OH$

Figure is too small to read but it shows the large number of Investigations and demonstrates how the results mainly cluster around the best fit line.
Illustrates the ideas of upper and lower bounds and of a probability distribution function (pdf)
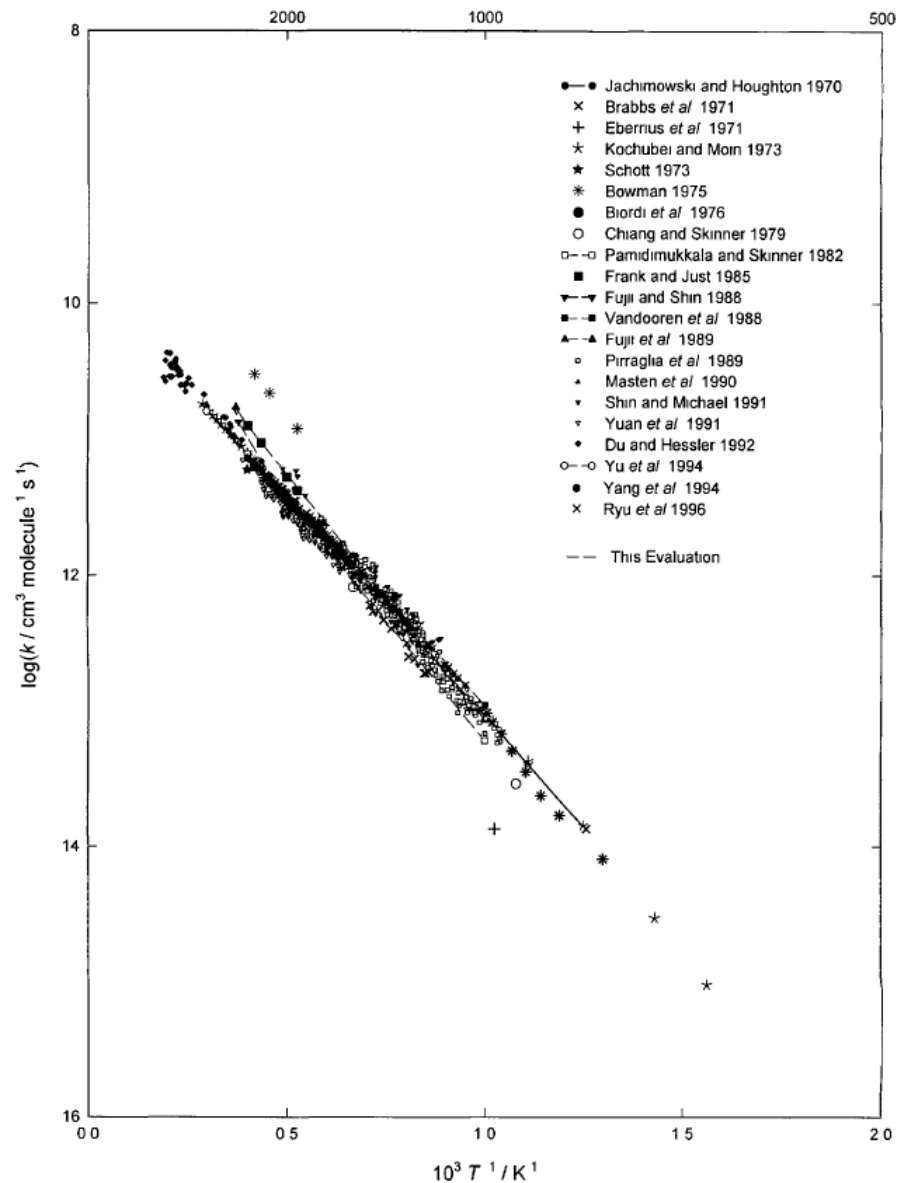
REMINDER: earlier slide on H + O$_2$ → OH + O

- From Hong et al., shock tube measurements. Comb Flame 2011, 158,633, $k = 1.7 \times 10^{-10}$ exp($-7670/T$) (1100 – 3370 K). Uncertainty ± 10%.

- See Burke et al. Int J Chem Kinet, 2012, 44, 444, who support the rate coefficient

$^3CH_2 + CH_3 \rightarrow C_2H_4 + H$ – an example with limited measurements

Rate Coefficient Data

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
$5 \cdot 10^{-11}$	298	Pilling and Robertson, 1975[1]	(a)
$1.0 \cdot 10^{-10}$	298	Laufer and Bass, 1975[2]	(b)
$3 \cdot 10^{-11}$	1800-2700	Olson and Gardiner, 1978[3]	(c)
$3 \cdot 10^{-11}$	1700-2200	Bhaskaran et al., 1979[4]	(d)
$(7-10) \cdot 10^{-11}$	1320-2300	Frank and Braun-Unkhoff, 1987[5]	(e)
$1.1 \cdot 10^{-10}$	298	Deters et al., 1998[6]	(f)
$1.7 \cdot 10^{-11}$	1350-2400	Hidaka et al., 2000[7]	(g)
$2.1 \cdot 10^{-10}$	298	Wang and Fockenberg, 2001[8]	(h)

7×10^{-11}, when most recent value for $k(CH_3+CH_3)$ used

Shock tube measurements used mechanisms with several steps and literature rate data
Not possible to correct for more recent values – emphasises need to store raw data to allow accurate re-evaluation

$^3CH_2 + CH_3$ continued

- k = $1.2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 298-3000 K.
- Δlog k = ± 0.3 at 298 K, rising to ± 0.7 at 3000 K.

Comments:

- Considerable scatter on the data at 298 K. The rate data of references 1 and 2, which were derived from very similar studies, need correction for the value of the rate constant for the methyl radical recombination used in the simulations.

- Reaction presumed to proceed via an ethyl radical adduct. A significant temperature dependence for k is therefore not expected, - supported by results from the shock tube studies. May suggest a very small negative temperature dependence, but scatter at high T large and, provisionally, a temperature independent k is recommended with substantial error limits.

Pressure dependent reactions - reminder

Troe Fitting

Need to represent k(T,P) for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F \qquad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\dfrac{\log_{10}(p^*)+c}{N - d(\log_{10}(p^*)+c)}\right]^2}$$

$$p^* = k_0[M]/k^\infty \qquad d = 0.14$$

$$c = -0.4 - 0.67\log_{10} F_{cent} \qquad N = 0.75 - 1.27\log_{10} F_{cent}$$

Fit k_0 & k^∞ to modified Arrhenius $\qquad k_0 = A_0 T^{n_0} \exp(-E_0/T)$

Fit F_{cent} to:

$$F_{cent} = (1-a)\exp\left(-T/T^{***}\right) + a\exp\left(-T/T^*\right) + \exp\left(-T^{**}/T\right)$$

Pressure dependent reaction: $H + C_2H_4$

- $k_0 = 1.3 \cdot 10^{-29} \exp(-380/T)$ cm^6 molecule^{-2} s^{-1} for M = He over the range 300-800 K.
- $k_0 = 1.3 \cdot 10^{-29} \exp(-380/T)$ cm^6 molecule^{-2} s^{-1} for M = N_2 over the range 300-800 K.
- $k_\infty = 6.6 \cdot 10^{-15} \ T^{1.28} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the range 200-1100 K.
- $F_c = 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$ for M = He and N_2 over the range 300-800 K.

Reliability
- $\Delta\log k_0 = \pm 0.3$ for M = He, N_2 over the range 300-800 K.
- $\Delta\log k_\infty = \pm 0.3$ over the range 200-1100 K.
- $\Delta F_c = \pm 0.1$ for M = He, N_2 over the range 300-800 K.

H + C2H4
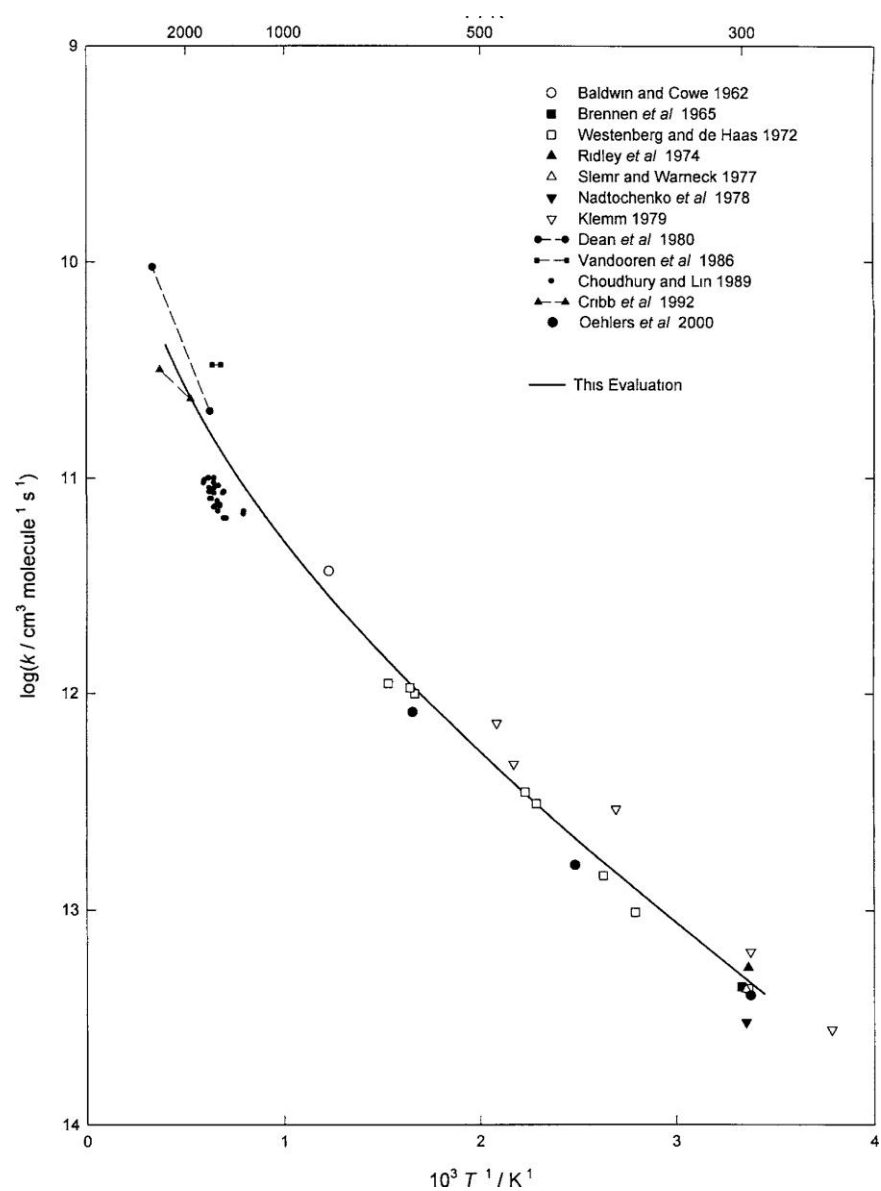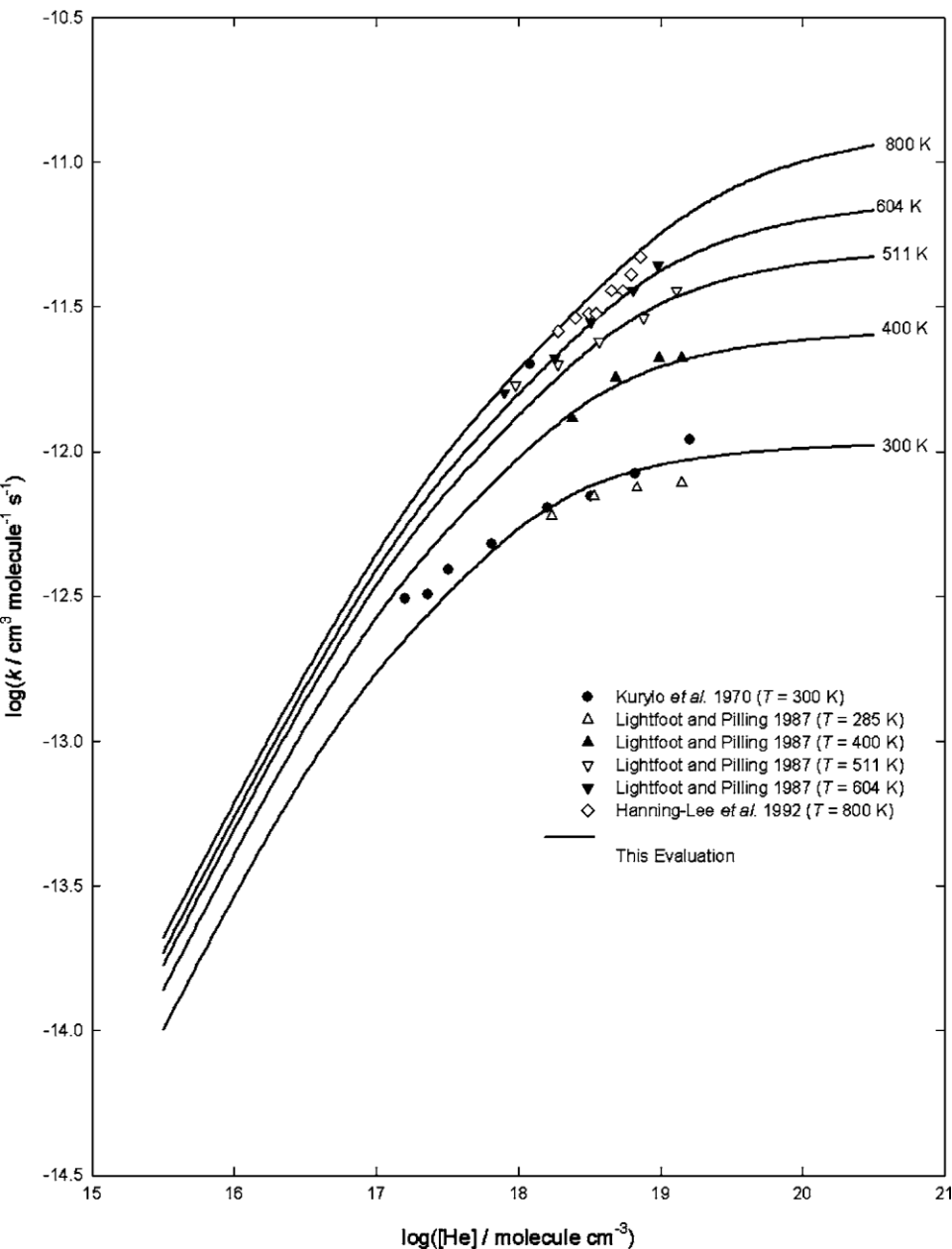
Nagy and Turanyi, Uncertainty of Arrhenius Parameters
Int J Chem Kinet 43: 359–378, 2011

- Analytical expression is derived that describes the temperature dependence of the uncertainty of k as a function of the elements of the covariance matrix of the Arrhenius parameters.

- Recommendations are given for an improved representation of the uncertainty information in future chemical kinetics databases using the covariance matrix of the Arrhenius parameters

- method suggested for determination of covariance matrix and joint probability density function of Arrhenius parameters from the present uncertainty information given in the kinetics databases.

O + C$_2$H$_4$: evaluation

O + C$_2$H$_4$ → CH$_2$CHO + H   (1)
      → HCO + CH$_3$ (2)
      → HCHO + CH$_2$ (3)
      → CH$_2$CO + H$_2$ (4)

- k = 2.25·10^{-17} $T^{1.88}$ exp(-92/T) cm^3 molecule^{-1} s^{-1} over the range 220-2000 K.

- Reliability

  Δlog k = ± 0.1 over the range 300-1000 K, rising to ± 0.3 at 220 K and 2000 K

O + $C_2H_4 \rightarrow$ products (Nagy and Turanyi)

$CH_3 + H \rightarrow {}^1CH_2 + H_2$
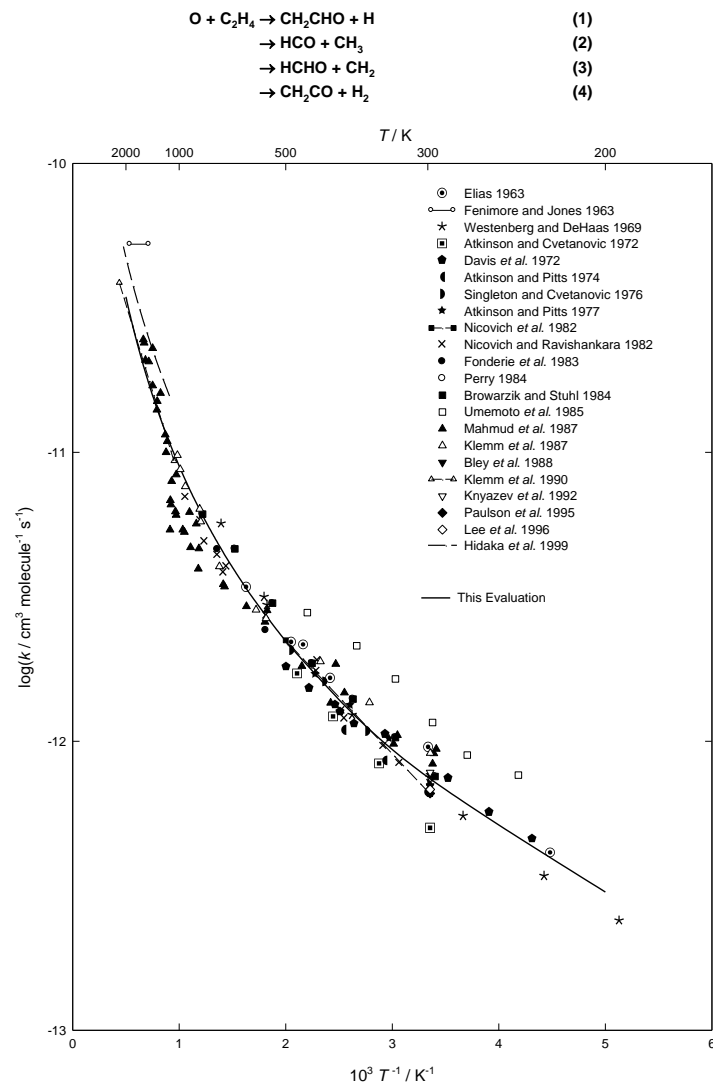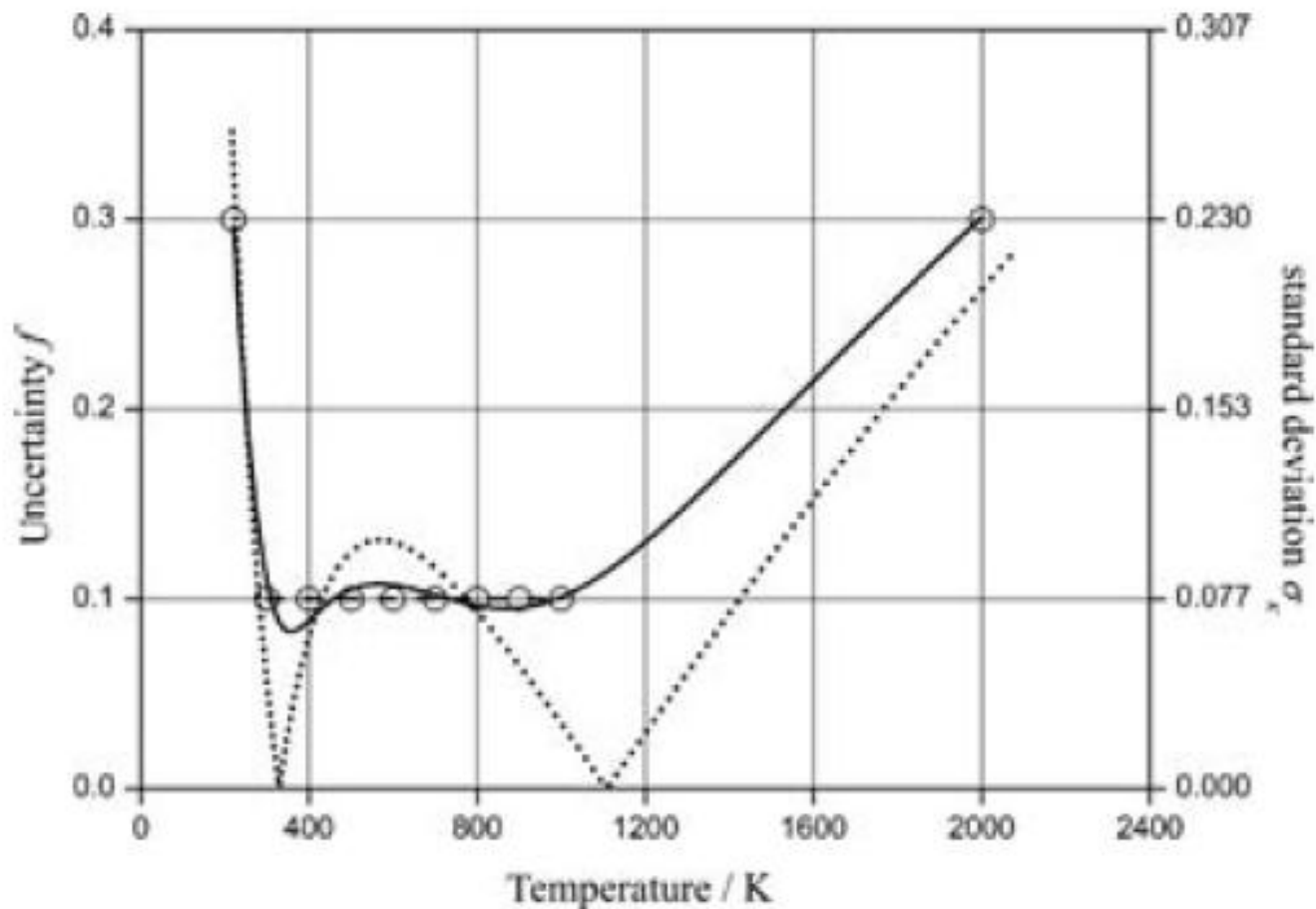
- $k = 2.1 \cdot 10^{-8}\ T^{-0.56} \exp(-8000/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the range 300-2500 K.

- Reliability

  $\Delta\log k = \pm 0.15$ over the range 300-1000 K, ± 0.3 over the range 1000-1700 K, and ± 0.2 over the range 1700-2500 K.

- Comments on Preferred Values

  The values of k obtained in the shock tube studies of Bhaskaran et al.[1] and Davidson et al.[3] are in reasonable agreement and also agree to within a factor of ~ 3 with the rate constants predicted by combining the thermodynamic data with the low temperature data on the reverse reaction, whereas the value of k obtained in the flame study of Langley and Burgess[2] seems unacceptably high.

T dependent uncertainty parameter, $k = AT^n \exp(-E/RT)$

- Covariance matrix:

$$\Sigma_{\mathbf{p}} = \overline{(\mathbf{p} - \bar{\mathbf{p}}) \, (\mathbf{p} - \bar{\mathbf{p}})^{\mathrm{T}}}$$

$$= \begin{bmatrix} \sigma_\alpha^2 & r_{\alpha n}\,\sigma_\alpha\,\sigma_n & r_{\alpha\varepsilon}\,\sigma_\alpha\,\sigma_\varepsilon \\ r_{\alpha n}\,\sigma_\alpha\,\sigma_n & \sigma_n^2 & r_{n\varepsilon}\,\sigma_n\,\sigma_\varepsilon \\ r_{\alpha\varepsilon}\,\sigma_\alpha\,\sigma_\varepsilon & r_{n\varepsilon}\,\sigma_n\,\sigma_\varepsilon & \sigma_\varepsilon^2 \end{bmatrix}$$

- Uncertainty parameter (M = 3/ln10 or 2/ln10) depending on definition of reliability in evaluation

$$F(T) = M\sqrt{\sigma_\alpha^2 + \sigma_n^2 \ln^2 T + \sigma_\varepsilon^2 T^{-2} + 2r_{\alpha n}\sigma_\alpha\sigma_n \ln T - 2r_{\alpha\varepsilon}\sigma_\alpha\sigma_\varepsilon T^{-1} - 2r_{n\varepsilon}\sigma_n\sigma_\varepsilon T^{-1}\ln T}$$

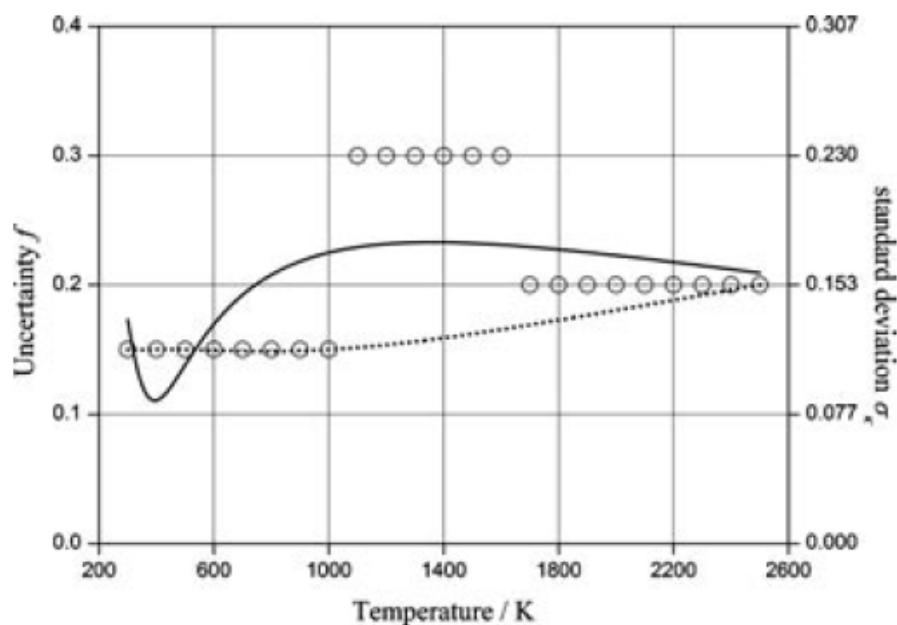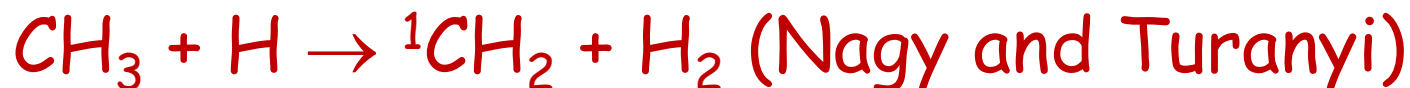# CH₃ + H → ¹CH₂ + H₂ (Nagy and Turanyi)

Figure 7 Uncertainties of reaction R5 are defined [14] in three temperature intervals and the uncertainty–temperature function was fitted to the values represented by the circles. The best least squares fit (solid line; see row **R5** in Table IV) does not approach these points well, because the recommended uncertainties were not consistent. The alternatively proposed $f(T)$ curve (dotted line) remains below all uncertainty points and has the highest average value of $\sigma_\kappa^2(T)$ in the inverse temperature interval of $[1/T_2, 1/T_1]$ (see text and row **R5m** in Table IV).

Uncertainty of the rate parameters of several important elementary reactions of the H_2 and syngas combustion systems (Nagy et al. Comb and Flame, 2015, 162, 2059)

- Re-evaluation of uncertainty parameters for 22 reactions using all available experimental and theoretical data.
- Based on lnA, n and E, uncertainty function, $f(T)$ stored as covariance matrix. $f(T)$ is the uncertainty range placed symmetrically about the mean rate constant.
- Discuss uncertainty in backward rate constant using forward rate constant and thermodynamics.
- A set of software tools is provided to allow the approach to be applied to any set of measured + calculated rate constants.
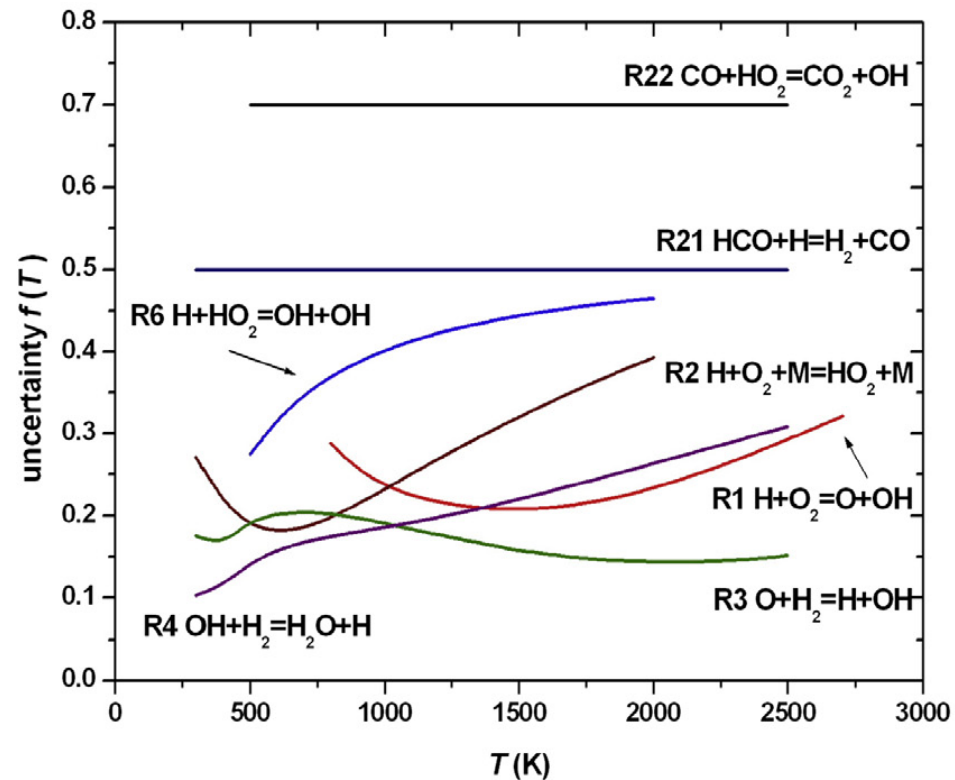
Examples of uncertainties for 7 of the 22 reactions studied. All taken from H_2 and syngas combustion mechanisms