



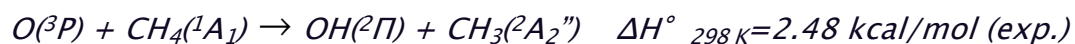
Practical session 1

Calculation of partition functions and macroscopic properties for a gas-phase reaction from ab initio electronic structure data

Ramón Sayós

1

Study of the *gas-phase elementary* reaction:



- Calculate optimal geometries (R, P and TS), energies and harmonic vibrational frequencies at **UMP2/6-311 G(d,p)** level
- Calculate the partition functions and the thermodynamic properties $S_i(T)$, $G_i(T)$, $Q_i(NVT)$, $\Delta G^\ddagger(T)$, $\Delta_r G^\circ(T)$, $\Delta_r S^\circ(T)$, $K(T)$ at $T = 0.001, 300, 600$ and 900 K and $P = 1 \text{ atm}$
- Calculate thermal rate constants by using Transition State Theory: $k(T)$ at $300, 600$ and 900 K
- Codes to use: **GABEDIT**, **GAMESS**, **KISTHELP** (with QUBUNTU)
GAMESS (in IQTCUB cluster)
- Inputs: **O.inp**, **CH4.inp**, **OH.inp**, **CH3.inp**, **TS.inp** (without symmetry)

2

Download the input files into QUBUNTU environment:

- 1) From **UAM (Moodle)** using your account
or
- 2) From IQTCUB cluster **cerqt2.qt.ub.edu** with your user:

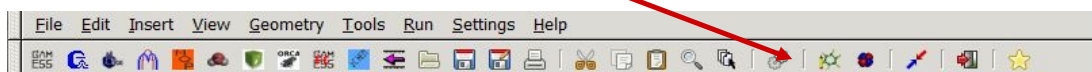
- open a terminal in QUBUNTU (use the *icon at bottom right*)
- **mkdir PS1** (create a directory)
- **cd PS1** (change to directory ps1)
- **scp your_user@cerqt2.qt.ub.edu:/work/MEAS/PS1/*.inp .**
(download all the files)
- check the files: **O.inp, CH4.inp, OH.inp, CH3.inp, TS.inp**
ls -la (in the terminal)
or
user>PS1 (open this folder with the mouse)

3

1. Calculations with **GABEDIT/GAMESS**:

A) Geometry optimization:

- Open GABEDIT: **applications > QC > Gabedit**
- Open the input file: **file > open > CH4.inp** (e.g. for CH₄)
- Run GAMESS: **run a program > Gamess** (check "exited gracefully")



- See in output file (**CH4.log**) energies and optimal geometry:
Look for ****** EQUILIBRIUM GEOMETRY LOCATED ******

4

GAMESS calculation using symmetry for CH₄

- 1) *Open CH4.inp with GABEDIT*
- 2) *Draw the last geometry in CH₄ optimization (without symmetry) from CH4.log:*
 - Select Geom. Conv > Draw (last point)*
- 2) *Use right button (mouse) over the plot > save as > XYZ file*
- 3) *Select: File > New > Gamess input*
- 4) *Select: Detected by Gabedit. (Td group)*
- 5) *Fill the other options as in CH4.inp calculation (i.e., same \$CONTRL and \$BASIS keywords):*
 - Equilibrium geometry, UHF, MP2, 6-311G, Direct SCF,..*
- 6) *Save the new input file as CH4_sym.inp*
- 7) *Run GAMESS again (valid for CH₄)*

D) Analyse the results:

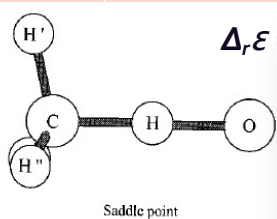
- Check the spin state (*SPIN SZ and S-SQUARED values*)
- Plot the vibrational normal modes (e.g., using *wxMacMolPlt*).
- Compare geometries and ν_i (R,P) with experimental data:

Species	Symmetry group	geometry (Å, °)	ν_i (cm ⁻¹)	σ
CH ₄ (¹ A ₁)	T _d	d _{CH} =1.091 <HCH = 109.47	1534.0 (2) 2916.5 1306.0 (3) 3018.7 (3)	12
CH ₃ (² A ₂)	D _{3h}	d _{CH} =1.079 <HCH = 120.0	580 1383 (2) 3002 3184 (2)	6
OH (² Π)	C _{∞v}	d _{OH} =0.9706	3846.6	1

(JANAF experimental data)

- Compare data for TS with published calculations.
- Calculate $\Delta \varepsilon^\ddagger$ and $\Delta_f \varepsilon$ (ε no internal energy !) with and without zero point energy correction.

Species	Symmetry group	geometry (Å, °)	ν_i (cm ⁻¹)	$\Delta \varepsilon^\ddagger$ (kcal/mol)
TS	$\approx C_{3v}$	$d_{OH}=1.206$ $d_{HC}=1.254$ $d_{H'C}=1.080$ $d_{H''C}=1.080$ $\angle H'CH = 104.7$	2259.0 i 238.8 377.0 624.4 1098.2 1139.4	1239.9 1367.2 1461.1 3116.7 3231.3 3276.0
				13.3 (9.4 with ZPE)



$$\Delta_r \varepsilon = 5.3 \text{ kcal/mol (1.3 with ZPE)}$$

Calculations in JCP 110 (1999) 7326:
(in Moodle)
PUMP4//UMP2/6-311G (3d2f, 3p2d)

9

- Do a table with $S_i(T)$, $G_i(T)$ and $Q_i(NVT)$ for all species at all T .
- Calculate $\Delta G^\ddagger(T)$, $\Delta_r G^\circ(T)$, $\Delta_r S^\circ(T)$ and $K(T)$ for all T :

$$\Delta_r G^\circ(T) = -RT \cdot \ln K$$

(you can use LibreOffice calc for the calculations)
- Compare with the experimental data (JANAF; in Moodle) for this reaction (1 bar, ideal gas):

T (K)	$\Delta_r S^\circ$ (cal/mol·K)	$\Delta_r G^\circ$ (kcal/mol)	K
0	-	1.8	0.05
300	7.3	0.3	0.6
600	8.8	-2.2	6.2
900	8.9	-4.8	15.0

$$E_a = 9.3, 10 \text{ kcal/mol (400-575 K)}$$

10

- Compare the energetic profiles using ϵ , with and without ZPE ($\epsilon \neq \epsilon(T)$) and $G(T)$ for this reaction, taking the zero of energy in reactants.

(you can use LibreOffice draw for the plots)

11

2. Calculations with **KISTHELP (2016)** (1 bar, gas ideal):

A) Calculation of $\Delta_r G^\circ(T)$, $\Delta_r S^\circ(T)$ and $K(T)$ for all T

- Prepare GAMESS outputs: change in the line **GAMESS VERSION** the year: **2014** \rightarrow **2012** and save the files:

(O_thermo.log, CH4_thermo.log, CH3_thermo.log, OH_thermo.log)

- Open KISTHELP: *Applications > QC > KiSThelp*
- *Session > New, Calculation > Keq ...* (read *_thermo.log files)

B) Calculation of $\Delta G^{\ddagger^\circ}(T)$, Q_i and thermal rate constants ($k(T)$) for all T

- Prepare TS_thermo.log file: **2014** \rightarrow **2012**
- Open KISTHELP
- Build a TS.kinp file: *Data > Build R°Path.kinp > 1 > TS_thermo.log > TS.kinp*
- *Session > New, Calculation > k/TST > Bimolecular > read files:*
O_thermo.log, CH4_thermo.log and TS.kinp

12

- *KISTHELP Inputs (name.kinp):*

O.kinp

```
*MASS (in amu)
15.99491
*END
*ELECTRONIC DEGENERACY
3
*END
*POTENTIAL ENERGY (in hartree)
-74.9225863972
*END
```

CH4.kinp

```
*MASS (in amu)
16.031280000000002
*END
*NUMBER OF SYMMETRY
1
*END
*FREQUENCIES (in cm-1)
1365.02
1365.07
1365.09
```



```
1582.68
1582.71
3074.08
3210.86
3210.91
3210.98
*END
*ELECTRONIC DEGENERACY
1
*END
*MOMENT OF INERTIA (in
Amu.bohr**2)
11.409810809550905
11.409811530894157
11.409918290701015
*END
*LINEAR
not linear
*END
*POTENTIAL ENERGY (in hartree)
-40.3805285792
*END
```

13

TS.kinp

```
**POINT
*IRC
0.0
*END
*MASS (in amu)
32.02619
*END
*NUMBER OF SYMMETRY
1
*END
*FREQUENCIES (in cm-1)
2205.48i
301.82
370.28
610.89
1063.41
1141.53
1243.64
1427.36
1463.47
3117.82
3264.81
3273.62
*END
```



```
*ELECTRONIC DEGENERACY
3
*END
*MOMENT OF INERTIA (in
Amu.bohr**2)
11.970291604905814
182.65114236519247
182.6918193949774
*END
*LINEAR
not linear
*END
*POTENTIAL ENERGY (in hartree)
-115.2685293939
*END
**END
```

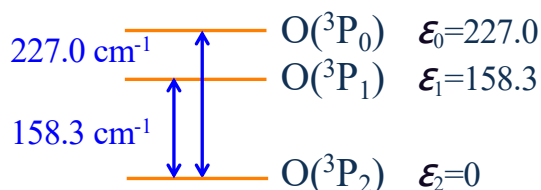
14

Questions and additional calculations:

- Which would be the effect into the chemical equilibrium if the total pressure increase until 2 bar?
- Calculate by hand q_O , S_O , q_{OH} and S_{OH} at 300 K using the appropriate formulas.
- Use the symmetry in GAMESS calculations (i.e., CH_3 and CH_4) and check again q_i values, σ and the classification of the vib. frequencies.
- Check the occupation of the spin-orbit electronic states of $O(^3P)$ at $T = 0$ and 300 K.

s-o states	ϵ (cm^{-1})
3P_2 (5 states)	0
3P_1 (3 states)	158.265
3P_0 (1 state)	226.977
1D_2 (5 states)	15867.862

JANAF experimental data



15

GAMESS calculation in IQTC cluster

–Steps:

- Connect to the cluster (ssh):
`ssh -l -X your_user cerqt2.qt.ub.edu (or ssh -Y)`
- Make a directory in your home:
`mkdir PS1`
- Copy input files (5) and script (1) from /work/MEAS into your home:
`cd PS1`
`cp /work/MEAS/PS1/*.`
- Send your calculation with GAMESS16 in a batch queue (e.g., for CH4.inp file put as name CH4):
`qsub -N name rungameess16 (send the calculation)`
`qstat (show the status of your job)`
- Show all available cluster software: `module_cerqt2 avail`

16

- To copy files from QUBUNTU to CERQT2 user's home:
scp name_of_file your_user@cerqt2.qt.ub.edu:/home/your_user
- To copy files from CERQT2 user's home to QUBUNTU current directory:
scp your_user@cerqt2.qt.ub.edu:/home/your_user/name_of_file .

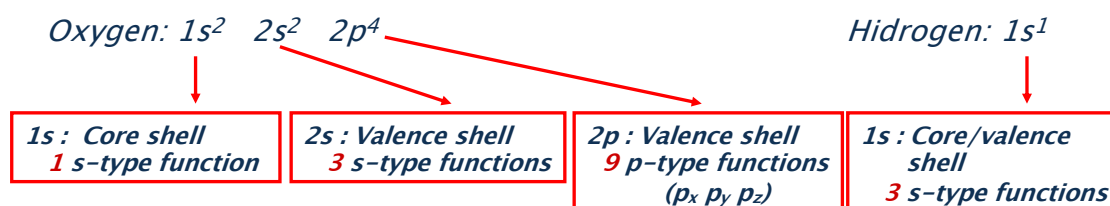
17

Additional slides

18

Pople basis sets

- Example: H_2O with a split-valence 6-311G basis set



$$H_2O: O (1+3+9) + H (3) + H (3) = 19 \text{ basis functions } (\Phi_i)$$

$$O (6+5+15) + H (5) + H (5) = 36 \text{ primitive functions } (\chi^{GTO}_i)$$

$$\phi_{2s} = \sum_{s=1}^3 c_s \chi_s = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3$$

$$\chi_1 \equiv \chi_1^{CGTO} = b_1 \chi_1^{GTO} + b_2 \chi_2^{GTO} + b_3 \chi_3^{GTO}$$

$$\chi_2 \equiv \chi_2^{CGTO} = b_4 \chi_4^{GTO}$$

$$\chi_3 \equiv \chi_3^{CGTO} = b_5 \chi_5^{GTO}$$

19

GTO: Gaussian Type Orbital

$$\chi_{n,l,m}^{GTO}(\vec{r}) = N \cdot r^l e^{-\alpha r^2} \cdot Y_{l,m}(\theta, \varphi) \quad , \quad \alpha > 0 \quad (\text{depends of } n \text{ and } l)$$

$$\chi_{s,t,u}^{GTO}(x,y,z) = N \cdot x^s \cdot y^t \cdot z^u \quad l = s + t + u \quad (\text{in cartesianes})$$

- 6-311G Pople basis set:** uses 1 basis function for each core orbital with 6 primitive gaussians, and 3 basis functions for each valence orbital with 5 primitive gaussians with a contraction of 3 +1 +1.

- Polarizations functions**

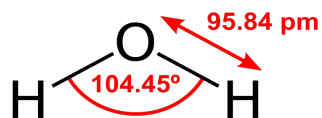
(d,p): means one set of 6 extra d-type orbitals for non-hydrogen atoms or one set of 3 p-type orbitals for H atoms.

20

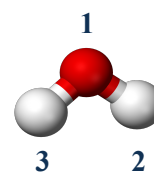
Z-matrix

– Example: H_2O (C_{2v}):

$d(OH)=0.9584 \text{ \AA}$
 $d(OH')=0.9584 \text{ \AA}$
 $\angle HOH'=104.45^\circ$



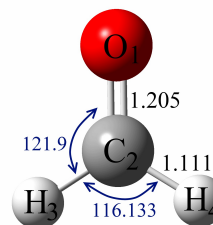
1	O					
2	H	1	0.9584			
3	H	1	0.9584	2	104.45	



21

– Example: Formaldehid (C_{2v}):

$d(OC)=1.205 \text{ \AA}$
 $d(CH)=1.111 \text{ \AA}$
 $d(CH')=1.111 \text{ \AA}$
 $\angle OCH=121.9^\circ$

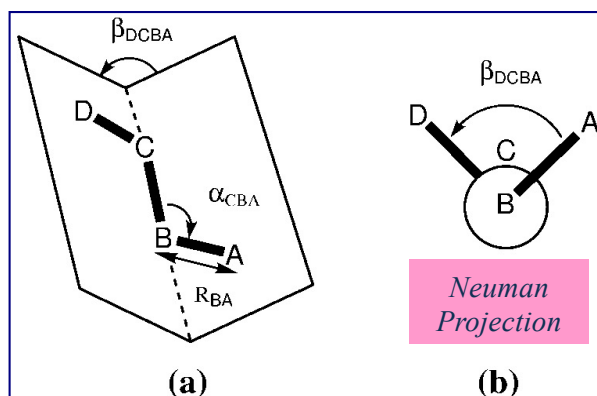


1	O					
2	C	1	1.205			
3	H	2	1.111	1	121.9	
4	H	2	1.111	1	121.9	3

Dihedral angle 4213

22

Dihedral angle (DCBA)



23

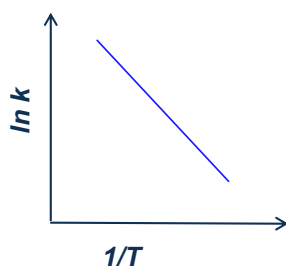
$$k = A \cdot e^{-E_a/RT}, \quad \ln k = \ln A - \frac{E_a}{RT}, \quad \frac{d \ln k}{d(1/T)} = -\frac{E_a}{R} \quad (\text{Arrhenius equation})$$

- A and E_a are empirical parameters:

A : Preexponential factor (units like k); does not depend on T

E_a : activation energy (energy units/mol); does not depend on T

T : temperature (units: K)



origin intercept = $\ln A$
slope = $-E_a/R$

24

- *Other empirical equations:*

$$k = A \cdot T^m \cdot e^{-B/T} \quad (\text{Kooij equation; 3 parameters: } A, B, m)$$

$$k = A \cdot T^m \quad (\text{Harcourt \& Esson; 2 parameters: } A, m)$$