

# Efforts for the database on plasma simulation at Athenasys

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# Company profile

Athenasys started in October 2008, as a consultant for customers in mainly semiconductor industry, and became an agent for CFD-ACE+ which is one of multi-physics software in 2009. And the company also started to work with Quantemol in 2012.

※ Before starting Athenasys, Ikeda worked at the ex-distributor of CFD-ACE+ and Anelva which was one of semiconductor equipment suppliers. Kobayashi worked at Anelva as well.

## Main software/database :

CFD-ACE+	(work with ESI Group, since 2009)
Quantemol-N	(work with Quantemol, since 2012)
Q-DB	(work with Quantemol, since 2017)

## Member of NPO

原子・分子応用フォーラム (Atom-Molecular data forum)

## Affiliation Society

JSAP, IEEJ, SCEJ



# Database for plasma simulation

## Species

Lennard-Jones parameter

Jannaf coefficient

\*consideration of energy balance with heavy particles

Polarizability

Charge exchange cross section

## Gas phase reaction (some open sources are available)

Rate constant, look up table\*, or cross section

(\*Athenasys is planning to release a tool to make a better look up table using propagator method)

## Surface reaction

Sticking coefficient (recombination/destruction probability)

\* depending on surface, temperature, ion energy



# Thermal data by NIST and Jannaf

Heat capacity( $C_p$ ), enthalpy ( $H$ ), and entropy( $S$ ) can be calculated by an equation of polynomial in temperature, but they are different in NIST and Jannaf.

Athenasys can convert the coefficients from NIST to Jannaf to input them into CFD-ACE+.

## NIST

### Gas Phase Heat Capacity (Shomate Equation)

$$C_p^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$$

$$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$$

$$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$$

$C_p$  = heat capacity (J/mol\*K)

$H^\circ$  = standard enthalpy (kJ/mol)

$S^\circ$  = standard entropy (J/mol\*K)

t = temperature (K) / 1000.

## Jannaf

$$\frac{C_p^\circ}{R} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4,$$

$$\frac{H_k^\circ}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{T_k},$$

$$\frac{S_k^\circ}{R} = a_{1k}\ln T_k + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k}.$$

These coefficients are usually found for only ground state. Simple assumption to estimate coefficients can be possible to shift the potential level using  $a_6$  in the case of Jannaf.



# A lot of states and complex chemistry

It is almost impossible to include every possible states, so that we need to choose some important states in the chemistry, while it also depends on the pressure and power.

Some excited states are difficult to measure electron collision cross section experimentally.

As a result, some kind of estimation or calculation is needed. Q-N is a good choice for it for molecules.

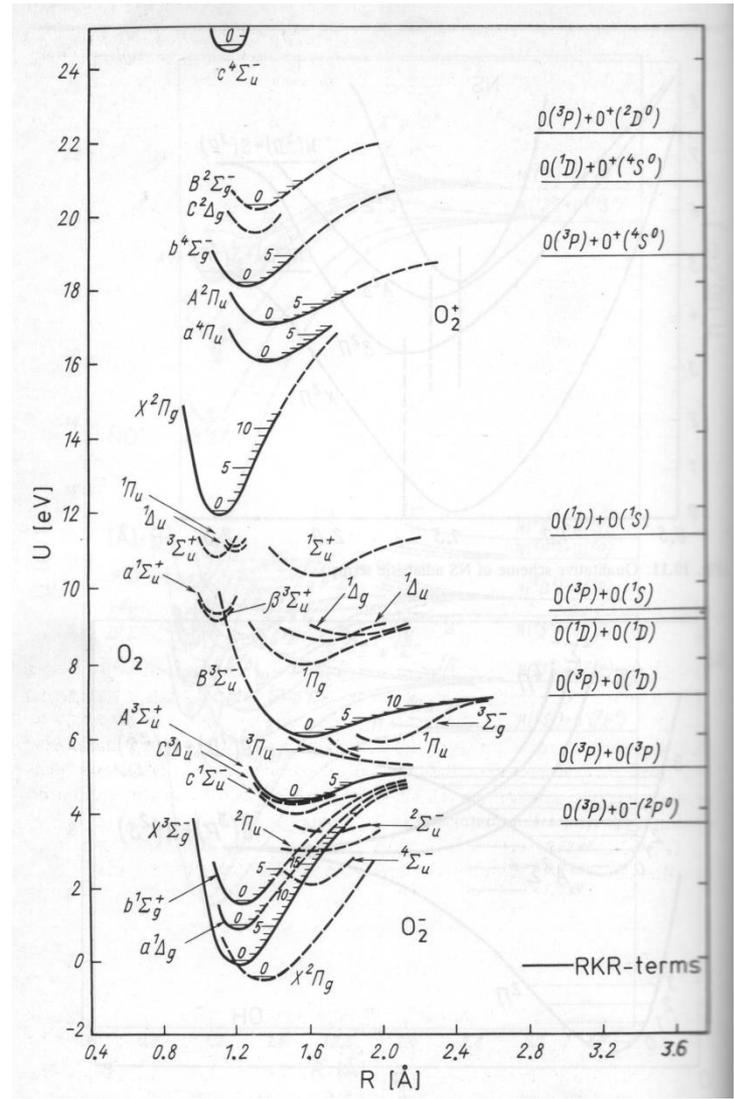


Fig. Potential energy curves for electronic states of O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup>



# A lot of states and complex chemistry(cont.)

Similar cross section curves :  $O_2$  and  $O_2(a^1\Delta_g)$

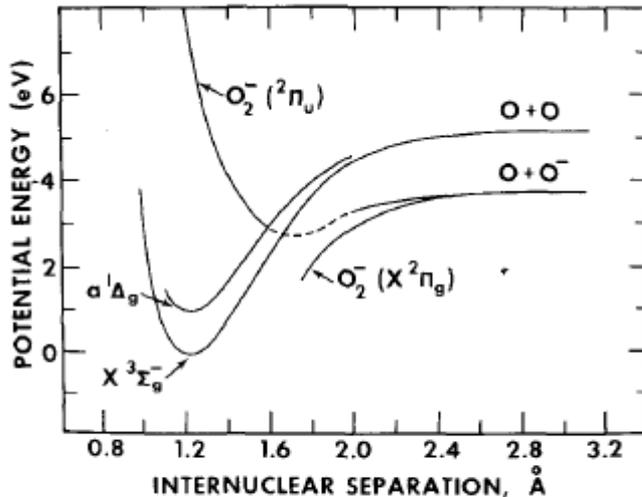


FIG. 5. Simplified diagram showing potential energy as a function of internuclear separation (from Ref. 5).

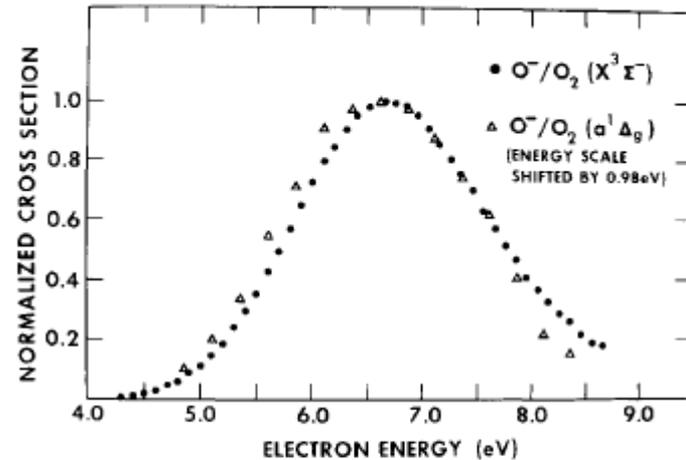


FIG. 6. The normalized cross sections for dissociative attachment from  $O_2(a^1\Delta_g)$  and  $O_2(X^3\Sigma_g^-)$  states as a function of electron impact energy. The  $a^1\Delta_g$  cross section has been shifted to higher energy by 0.98 eV and modified as described in the text.

P. D. Burrow, Dissociative attachment from the  $O_2(a^1\Delta_g)$  state \*, J. Chem. Phys. 59, 4922 (1973)

In some cases, it could be possible to assume cross section by shifting the threshold and multiply the values using another state, it is not always though. But to learn how to estimate is also valuable.



# A lot of states and complex chemistry(cont.)

## Global model by J T Gudmundsson for O<sub>2</sub>

J. Phys. D: Appl. Phys. 34 (2001) 1100–1109

**Table 1.** The reaction set for oxygen. The rate coefficients for electron impact collisions were calculated assuming Maxwellian electron energy distribution and fitted over an electron temperature range 1–7 eV.

Reaction	Rate coefficient	Reference
$e + O_2 \rightarrow O_2^+ + 2e$	$k_1 = 9 \times 10^{-16} T_e^{2.0} \exp(-12.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[23]
$e + O_2^+ \rightarrow O(^3P) + O(^3P)$	$k_2 = 2.2 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O_2 \rightarrow O(^3P) + O^-$	$k_3 = 8.8 \times 10^{-17} \exp(-4.4/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O(^3P) \rightarrow O^+ + 2e$	$k_4 = 9.0 \times 10^{-15} T_e^{0.7} \exp(-13.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$O^- + O_2^+ \rightarrow O(^3P) + O_2$	$k_5 = 1.5 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[23]
$O^- + O^+ \rightarrow O(^3P) + O(^3P)$	$k_6 = 2.7 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O^- \rightarrow O(^3P) + 2e$	$k_7 = 1.1 \times 10^{-13} \exp(-3.58/T_e) \text{ m}^3 \text{ s}^{-1}$	[47]
$e + O_2 \rightarrow O(^3P) + O(^3P) + e$	$k_8 = 7.1 \times 10^{-15} \exp(-8.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[11]
$O(^3P) + O^- \rightarrow O_2 + e$	$k_9 = 3.0 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2 \rightarrow O^- + O^+ + e$	$k_{10} = 7.1 \times 10^{-17} T_e^{0.5} \exp(-17/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2 \rightarrow O(^3P) + O^+ + 2e$	$k_{11} = 5.3 \times 10^{-16} T_e^{0.9} \exp(-20/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$O^+ + O_2 \rightarrow O(^3P) + O_2^+$	$k_{12} = 2 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O_2 \rightarrow O(^3P) + O(^1D) + e$	$k_{13} = 1.8 \times 10^{-13} \exp(-18.33/T_e) \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O(^3P) \rightarrow O(^1D) + e$	$k_{14} = 4.5 \times 10^{-15} \exp(-2.29/T_e) \text{ m}^3 \text{ s}^{-1}$	[23]
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$k_{15} = 3.0 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$	[11]
$O(^1D) + O(^3P) \rightarrow 2O(^3P)$	$k_{16} = 8.1 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$	[23]
$e + O(^1D) \rightarrow O^+ + 2e$	$k_{17} = 9 \times 10^{-15} T_e^{0.7} \exp(-11.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[23]
$e + O_2 \rightarrow O_2(a^1\Delta_g) + e$	$k_{18} = 1.7 \times 10^{-15} \exp(-3.1/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2(a^1\Delta_g) \rightarrow O_2^+ + 2e$	$k_{19} = 9.0 \times 10^{-16} T_e^2 \exp(-11.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2(a^1\Delta_g) \rightarrow O^- + O$	$k_{20} = 2.28 \times 10^{-16} \exp(-2.29/T_e) \text{ m}^3 \text{ s}^{-1}$	[30]
$e + O_2(a^1\Delta_g) \rightarrow O_2 + e$	$k_{21} = 5.6 \times 10^{-15} \exp(-2.2/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2(a^1\Delta_g) \rightarrow 2O + e$	$k_{22} = 4.2 \times 10^{-15} \exp(-4.6/T_e) \text{ m}^3 \text{ s}^{-1}$	[46]
$O^- + O_2(a^1\Delta_g) \rightarrow O_2^- + O(^3P)$	$k_{23} = 1.1 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[41]
$O_2^- + O_2^+ \rightarrow O_2$	$k_{24} = 2.0 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[46]

$O_2^- + O^+ \rightarrow O_2 + O(^3P)$	$k_{25} = 2.0 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[46]
$e + O_2 + O_2 \rightarrow O_2^- + O_2$	$k_{26} = 2.26 \times 10^{-42} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[48]
$O^- + O^+ \rightarrow O(^3P) + O(^1D)$	$k_{27} = 4.9 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[43]
$O_2^- + O_2(a^1\Delta_g) \rightarrow 2O_2 + e$	$k_{28} = 2.7 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[41]
$O_2^- + O(^3P) \rightarrow O^- + O_2$	$k_{29} = 3.31 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O_3 \rightarrow O^- + O_2$	$k_{30} = 9.3 \times 10^{-16} T_e^{0.62} \text{ m}^3 \text{ s}^{-1}$	[45]
$e + O_3 \rightarrow O + O_2^-$	$k_{31} = 2.0 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$	[45]
$O^- + O_2 \rightarrow O_3 + e$	$k_{32} = 5.0 \times 10^{-21} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[12]
$O^- + O_2(a^1\Delta_g) \rightarrow O_3 + e$	$k_{33} = 2.2 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[41]
$O^+ + O_3 \rightarrow O_2^+ + O_2$	$k_{34} = 1.0 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[46]
$O + O_3 \rightarrow 2O_2$	$k_{35} = 2.0 \times 10^{-17} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[46]
$O^- + O_3 \rightarrow O_3^- + O$	$k_{36} = 5.3 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$O_3^- + O(^3P) \rightarrow O_2^- + O_2$	$k_{37} = 3.2 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[12]
$O_3^- + O(^3P) \rightarrow 2O_2 + e$	$k_{38} = 3.0 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[12]
$O_3^- + O_2^+ \rightarrow O_2 + O_3$	$k_{39} = 2 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$O_3^- + O_2^+ \rightarrow 2O + O_3$	$k_{40} = 1.01 \times 10^{-13} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$O_2^- + O_3 \rightarrow O_2 + O_3^-$	$k_{41} = 4 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$O_2^- + O(^3P) \rightarrow O_3 + e$	$k_{42} = 3.01 \times 10^{-16} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O_3 \rightarrow O(^3P) + O_2 + e$	$k_{43} = 1 \times 10^{-14} (300/T_e)^{1/2} \text{ m}^3 \text{ s}^{-1}$	[11]
$2O_2 + O(^3P) \rightarrow O_3 + O_2$	$k_{44} = 6.9 \times 10^{-40} (300/T_e)^{-1.25} [O_2] \text{ m}^3 \text{ s}^{-1}$	[11]
$O_2^- + 2O(^3P) \rightarrow O_3 + O(^3P)$	$k_{45} = 3.82 \times 10^{-40} [O] \text{ m}^3 \text{ s}^{-1}$	[11]
$e + O(^3P) + O_2 \rightarrow O_2^- + O(^3P)$	$k_{46} = 1 \times 10^{-43} \text{ m}^6 \text{ s}^{-1}$	[11]
$e + O(^3P) + O_2 \rightarrow O^- + O_2$	$k_{47} = 1 \times 10^{-43} \text{ m}^6 \text{ s}^{-1}$	[11]
$e + O_2^+ \rightarrow O(^1D) + O(^3P)$	$k_{48} = 2.11 \times 10^{-13} (300/T_e)^{0.7} \text{ m}^3 \text{ s}^{-1}$	[11]
$O_2^+ + O(^1D) \rightarrow O_2(a^1\Delta_g) + O(^3P)$	$k_{49} = 1.0 \times 10^{-18} (300/T_e)^{0.5} \text{ m}^3 \text{ s}^{-1}$	[11]

This model can be good enough for lower pressure discharges, but it is not sufficient for atmospheric pressure discharge because a lot of additional species are generated in the gas phase



# A lot of states and complex chemistry(cont.)

A lot of reaction steps on  $O_3$  in  $O_2$

※  $O_3$  generations/decompositions strongly depend on temperature.

It is necessary to consider some important steps with temperature dependence at higher pressures.

※ 3<sup>rd</sup> body also plays an important role at higher pressure discharges.

表1 酸素中のオゾン生成過程①

反応式	速度定数 2分子反応: $\text{cm}^3/\text{molecule}/\text{sec}$ 3分子反応: $(\text{cm}^3/\text{molecule})^2/\text{sec}$
$e+O_2 \rightarrow O_2(B^3\Sigma_u^-)+e$ $O_2(B^3\Sigma_u^-)+M \rightarrow O+O(^1D)+M$	電子衝突反応の速度定数は換算電界強度の関数
$e+O_2 \rightarrow O_2(A^3\Sigma_u^+)+e$ $O_2(A^3\Sigma_u^+)+M \rightarrow O+O+M$	
$e+O_2 \rightarrow O_2(b^1\Sigma_u^+)+e$	
$e+O_2 \rightarrow O_2(a^1\Delta_g)+e$	
$e+O_2 \rightarrow O_2^++e+e$	
$e+O_2 \rightarrow O+O^-$	
$e+O_2^+ \rightarrow O(^1D)+O_2(a^1\Delta_g)$	
$O(^1D)+O_2 \rightarrow O_2(b)+O$	
$O(^1D)+O_2 \rightarrow O_2(a)+O$	$1.6 \times 10^{-12} \exp(67/T)$ $(1.2 \times 10^{-12})$
$O(^1D)+O_2 \rightarrow O_2+O$	$4.8 \times 10^{-12} \exp(67/T)$
$O(^1D)+O \rightarrow O+O$	$8.0 \times 10^{-12}$
$O+O_2+O_2 \rightarrow O_3+O_2$ $O+O_2+O_2 \rightarrow O_3^*+O_2$	$6.2 \times 10^{-34} (T/300)^{-2}$ $6.4 \times 10^{-35} \exp(663/T)$
$O+O_2+O \rightarrow O_3+O$ $O+O_2+O \rightarrow O_3^*+O$	$8.7 \times 10^{-35} (T/300)^{-2}$ $2.15 \times 10^{-34} \exp(345/T)$
$O+O_2+O_3 \rightarrow O_3+O_3$ $O+O_2+O_3 \rightarrow O_3^*+O_3$	$1.40 \times 10^{-33} (T/300)^{-2}$ $1.40 \times 10^{-33} (T/300)^{-2}$
$O_3^*+O \rightarrow O_2+O_2$	$1.5 \times 10^{-11}$
$O_3^*+O \rightarrow O_3+O$	$1.0 \times 10^{-10}$
$O_3^*+O_2 \rightarrow O_3+O_2$	$1.0 \times 10^{-14}$
$O_3^*+O_3 \rightarrow O_3+O_3$	0.0
$O+O+O_2 \rightarrow O_2+O_2$	$1.30 \times 10^{-32} (T/300)^{-1} \exp(-170/T)$
$O+O+O \rightarrow O_2+O$	$6.20 \times 10^{-32} \exp(-750/T)$

※ And more ...

# Better look up table (LUT)

Cross section data is ideal for accurate computations, but employing LUT is a sort of trends recent years.

The reasons are

- 1) It is possible to take an effect of non Maxwellian distribution into account
- 2) Faster than using cross section

Recent years, bolsig+ is one of popular tools to generate LUT. But the two-term approximation is not so good enough for some cases. Calculation for the look up table using Monte Carlo method is another option, but it also takes a long time to calculate it.

Propagator method for calculations of electron transport parameters can be enough accurate as Monte Carlo method and still enough fast to calculate it. We are currently working with a professor Sugawara on this.



# Conclusions

Efforts at Athenasys for the database on plasma simulation :

- To find and provide species data as much as possible
- To provide cross section data with Quantemol
- Provide better look up table (in the near future)
- To provide reaction sets with Quantemol
- To help customers as a consultant with CFD-ACE+ Plasma