CHEMICAL REACTIONS LEARNING OBJECTS

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Introduction

The Virtual Education Community (VEC) Commission and the **EChemTest®** work group at their meeting during the recent ECTN Association [http://ectn.eu/] General Assembly held in Prague on April 2018 have urged a more active participation of the Association members to populate Question & Answer (Q&A) Libraries of **EChemTest®** and the GLOREP (Grid Learning Object) repository with Learning Objects (LO)s according to the prosumer model [1]. The Department of Chemistry, Biology and Biotechnologies, University of Perugia, delivers to the students of its Master degree in Chemical Sciences (that is part of the Erasmus Mundus (EM) Master Degree in Theoretical Chemistry and Computational Modelling (TCCM) [https://tccm.qui.uam.es/] in a Consortium of seven European Universities coordinated by the Universidad Autonoma de Madrid and accredited by ECTN as Euromaster®) a course on theory and computing of chemical reactions. Based on the lectures delivered to the students of that course (CHEMREA), A. Laganà and G.A. Parker have Published for Springer the book "Chemical Reactions: basic theory and computing". According to the mentioned prosumer model, CHEMREA is articulated in LOs meant to be made available in GLOREP for further collaborative development.
The LOs have been produced in collaboration with the Innovation Educational Office & E-learning Lab (LABEL) of the University of Perugia. Due to its focus on Educational activities, LABEL works on the production, post-production and delivery of Digital Didactic Objects as well as on the development and management of specialized E-learning platforms. LABEL supports also Research activities, ranging from the use of new technologies to the experimenting of innovative teaching methodologies. In this spirit, the LABEL Staff assists teachers in the initial analysis of their needs, in the design and planning of new digital products and actively contributes to the development of innovation. Relevant work is published using proprietary web platforms, social networks, webTV and the European M.O.O.Cs Consortium "EDUOPEN". Learning Objects produced for CHEMREA have been implemented according to specific pedagogical criteria for online learning and employing LABEL specialized personnel and technologies [2]. The present paper illustrates first the sections of the book that have been considered for building LOs, second the technologies used for assembling audiovisuals out of them and third the details of the first LO of the series.

1. The CHEMREA Learning Objects

In GLOREP some basic tools are provided for the production, storage and improvement of LOs through the use of the search, retrieval and management functions of the distributed repository [http://services.chm.unipg.it/ojs/index.php/virtlcomm/article/view/106] with the main features of the LOs being self-consistency, modularity, availability, reusability, interoperability. LOs, therefore, can be stand alone products or can be aggregated to the end of generating a more complex product. They can be made readily available thanks to the use of metadata.
The use of metadata allows, in fact, the cataloguing and classification of LOs according to the information content and any other factor they contain. The use of metadata allows us also to verify the existence of a LO and to locate it unambiguously.
In GLOREP metadata is used in a hierarchical way (more commonly known as schemas or ontologies) that connects the various components of the resources for an adequate and full

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fruition. This is often performed through the mapping of different metadata schemas. These schemas also provide data for identifying and localizing the resource. In the context of a repositories network, the choice of metadata ensures the interoperability between different types of resources (text, audio, video, etc..) and the integration of various information systems by indexation with a uniform metadata schema. This can be implemented both within and outside the single repository and makes the choice of the metadata schema to adopt crucial. When trying to transform the concept of "sharing" into the concept of "continuous training" (life long learning), it can be created a structured network, available online and produced by the users themselves, with the hope of diffusing didactic models. The models can be used like a guide, replicable in different academic European contexts, to suggest innovative pedagogical aspects, tools and production techniques aimed at the realization of LOs. Careful coordination and correct archiving of the educational material produced by the different Universities participating in the project could be included within the network used for the provision of the Quizzes and thus constitute an important basis for science sharing.
For this purpose CHEMREA has been partitioned in 18 LOs corresponding to 4 blocks (LO 1, LO 2, LO 3, LO 4) entitled respectively: From the phenomenology of chemical reactions to the study of two body collisions, The quantum approach to the two-body problem, Ab initio electronic structure for few-body systems, and The treatment of few-and multi-body reactions. The four blocks are articulated as follows:

1-From the phenomenology of chemical reactions to the study of two body collisions
LO 1.1 From Kinetics to Bimolecular Collisions (The phenomenological approach, Realistic kinetic models, The Transition State Theory approach, Towards detailed single collision studies)
LO 1.2 Classical mechanics of two particle collisions (Reference frame and elementary interactions, The equations of motion, The deflection angle θ)
LO 1.3 The computation of scattering properties (Trajectories integration (Hamilton equations), Numerical computation of the deflection angle θ, Other collisional properties, The cross section)
LO 1.4 Popular scattering model potentials (The rigid sphere model, The Repulsive Coulomb potential, Sutherland and Morse attractive-repulsive potentials, The scattering Lennard-Jones (6-12) potential)

2-The quantum approach to the two-body problem
LO 2.1 Quantum mechanics and bound states (The limits of the classical mechanics approach The 3D quantum problem and its decomposition, The Harmonic Oscillator)
LO 2.2 Quantum elastic scattering (The Coulomb potentials and the hydrogen atom, The formulation of quantum elastic scattering, The quantum elastic scattering cross section)
LO 2.3 Realistic Models for scattering systems (Continuum solutions for hydrogen-like atoms E>0, The rigid sphere, The Morse potential)
LO 2.4 Numerical integration of the Schrödinger equation (Expectation values of the operators, Approximation to the Laplacian, Approximating the wave function, The approximation to the potential)
LO 2.5 Numerical applications (Systems of linear algebraic equations, The structure of the wavefunctions, The Time-Dependent method)

3-Ab initio electronic structure for few-body systems
LO 3.1 Structured Bodies (The one-electron wavefunction approach, Quantum Monte Carlo, Many electron wavefunctions, The electronic structure of molecules)
LO 3.2 Higher Level ab initio Methods (Beyond the Hartree-Fock method, The CI and MC-SCF methods, Perturbation methods)
LO 3.3 Towards extended applications (Computation of other molecular properties, Density Functional Theory methods, The valence electron method, Dropping multicenter integrals)
LO 3.4 Full range process potentials (The three body internuclear coordinates, Global formulation of the potential energy surface

4. The treatment of few-and multi-body reactions

LO 4.1 The combined dynamics of electrons and nuclei (The N body dynamical equations, A direct integration of the general equations, The Born-Oppenheimer approximation)
LO 4.2 Three atom systems (Three body orthogonal coordinates, Atom-diatom reactive scattering Jacobi method, Atom-diatom time independent APH method, The atom-diatom time-dependent APH method)
LO 4.3 Beyond full quantum calculations (Reduced dimensionality quantum treatments, Leveraging on classical mechanics, Semiclassical treatments)
LO 4.4 Basic features of atom-diatom reactions (Energy dependence of the detailed probabilities, Quantum effects, Experimental observables, Periodic orbits and statistical considerations, The last mile to the experiment)
LO 4.5 Towards more complex systems (Full range Ab initio PESs for many body systems, Fitting PESs for reactive and non reactive channels, Four atom Many Process Expansion, Four atom quantum and quantum-classical dynamics, Last mile calculations for crossed beam experiments)

2. The adopted technology for audiovisual Learning Objects

The process technology adopted can be articulated into seven different stages: Analysis, Design, Production, Post-Production, Testing, Delivery and Management. This production chain can bring qualitatively different results according to three factors: 1) educational design, 2) technologies, 3) technical skills. In fact, while maintaining the design as the most important phase for the effectiveness of the final result, the use of professional and innovative technologies and the presence of technically specialized personnel still have an important role in the process. Three levels of equipment are, therefore, proposed (basic, middle, upper) leveraging the same basic level set up characterized by the presence of a computer, an audio/video input and a video editing software.

BASIC LEVEL:
Notebook, Integrated webcam, 8GB, 1 TB HDD, HDMI, USB 3.0 (about 450 €)
- n.1 recording audio/video opensource software (free)
- n.1 editing video opensource software (free)
OPTIONAL:
- n.1 professional Webcam, FULL-HD quality, recording optimized for recording and streaming, automatic corrections of light plus tripod (about 200 €)
- n.1 software for audio and video recording and editing (about 200 €)

MIDDLE LEVEL:
PC desktop for acquisition and editing (about 1000 €)
- n.1 Slide Remote control (about 50 €)
- n.1 Professional camera fullHD (about 1300 €)
- n.1 Static professional easel for camera (about 300 €)
- n.4 LED lighthouse for lightening recording room (about 500 €)
- n.1 Acquisition video card (about 500 €)
- n.1 Notebook, minimal requisites integrated webcam, RAM 8GB, HDD 1TB, HDMI, USB3.0 (about 450 €)
- n.1 Lavalier microphone + transmitter + receiver (about 150 €)
- n.1 Wireless stick microphone with receiving base (about 120 €)
- n.1 External audio acquisition card, USB, 2 inputs (about 150 €)
- wiring (HDMI and CANON wires + connectors) depending on the dimension of the recoding room.

UPPER LEVEL
Acquisition computer (about 1200 €)
- n.1 Slide Remote control (about 1200 €)
- n.1 Audio/video mixer, minimum 4 inputs (from 1800€ to 8000€)
- n.2 Professional camera 4K (about 5000 €)

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- n.2 Static professional easel for camera (about 700 €)
- n.8 LED lighthouse for lightening recording room (about 1000 €)
- n.1 Notebook (minimal specification: integrated WEBCAM RAM 16GB, HDD 1TB, HDMI, USB3.0) (about 800 €)
- n.2 Lavalier microphone + transmitter + receiver (about 250 €)
- n.1 Wireless stick microphone with receiving base (about 120 €)
- n.1 External audio acquisition card (USB, 2 inputs) (about 150 €)
- wiring (HDMI and CANON wires + connectors) depending on the dimension of the recoding room.

OPTIONAL:
- n.1 Tablet (about 400 €)
- n.1 Professional external audio acquisition card multi-input (about 1000 €)
- n.1 Computer for video editing (about 2500 €)

3. An example: LO 1-1

For illustrative purposes we show here the case of Learning Object From Kinetics to Bimolecular Collisions:

RATE OF CHEMICAL PROCESSES

- Isolated (no energy exchanged), Closed (no mass exchanged) and Open systems
- From hetero- to homo-geneous systems
- Gas phase P, V, T thermodynamics variables
- PV/T=costant
- The reactive process $A \rightarrow C$ (generalized $\alpha A+\beta B+\ldots \rightarrow \gamma C+\delta D+\ldots$)
- Reaction rate $v(t)=-d[A]/dt =d[C]/dt$ (generalized $v(t)=-d[A]/\alpha dt=-d[B]/\beta dt=d[C]/\gamma dt=d[D]/\delta dt$)

REACTION ORDER AND RATE COEFFICIENTS

- Order (the exponent of the power expression)
  $v = -d[A]/dt = k[A]^m$ order m
- If m=0 $k= ([A]_o-[A]_t)/(t-t_o)$
- If m=1 $k= (\ln[A]_o-\ln[A]_t)/\alpha\ (t-t_o)$
- If m>1 $k= (1/[A]_t^{m-1}-1/[A]_o^{m-1})/\alpha\ m(t-t_o)$

- for the generalized reaction $v = -d[A]/dt = k[A]^m[B]^n$ (order is $m+n$)

EVALUATION OF RATE COEFFICIENTS

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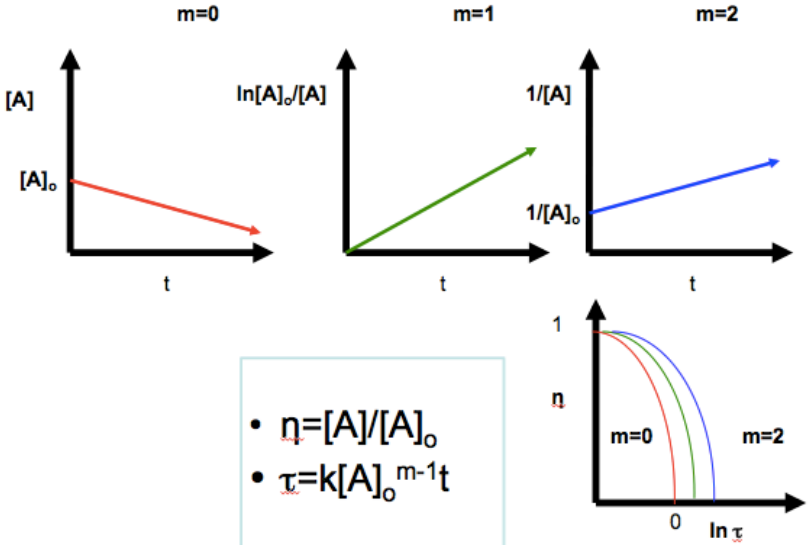
- Rate coefficients can be evaluated by measuring the varation of the concentration of either the reactants Δ[A] (or the products Δ[C]) as a function of the variation of time Δt given an initial concentration $[A]_o$
- Concentrations are measured in terms of either chemical (only for sufficiently slow reactions) or physical (pressure, spectra, conductivity, etc.) properties
- For simple reactions $v(t) = -d[A]/dt = k[A]^m$ the rate coefficient k can be estimated from Powell diagrams

POWELL DIAGRAMS



- $\eta=[A]/[A]_o$
- $\tau=k[A]_o^{m-1}t$

H_2 COMBUSTION REALISTIC MODEL

- For the reaction $2H_2+O_2 \rightarrow H_2+2OH \rightarrow 2H_2O$
- The Rate coefficient $v(t) = d[H_2O]/dt = k_2[OH][H_2]$ cannot be determined using the POWELL plots (as it happens for the vast majority of reactions) due to its more complex nature
- In this case one has to consider, instead, the different simpler processes (elementary processes) producing and connecting various stable intermediates (reaction mechanism) according to a combination of chained, branched, parallel, opposite, etc. steps
- Furthermore it has to be considered that the Rate coefficient k depends on the temperature T (k(T))

THE H_2 + O_2 REACTION MECHANISM

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Reaction	Role
$H_2+O_2 \rightarrow 2OH$, $H+HO_2$	(1) Initiation
$H_2+OH \rightarrow H+H_2O$	(2) Propagation
$H_2+HO_2 \rightarrow OH+H_2O$	Propagation
$H+O_2 \rightarrow OH+O$	(3) Chain branching
$H_2+O \rightarrow OH+H$	(4) Chain branching
$H+O_2+M \rightarrow HO_2+M$	(5) High press. termination
H,O,OH,→wall	(6) Low press. termination
$H+O_2+H_2 \rightarrow H+H_2O_2$	Restore chain at high T
$2HO_2 \rightarrow H_2O_2+O_2$	Restore chain at high T
$H_2O_2 \rightarrow 2OH$	Restore chain at high T

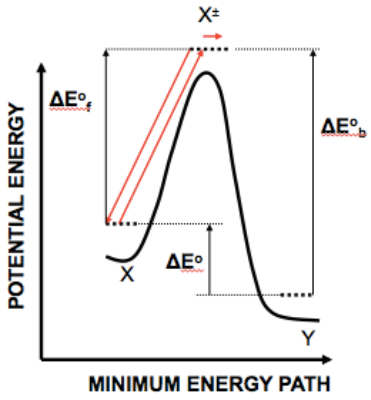
STATIONARY STATES OF OH, H, O

- $d[OH]/dt = 2k_1[H_2][O_2] - k_2[OH][H_2] + k_3[H][O_2] + k_4[O][H_2] = 0$
- $d[H]/dt = k_2[OH][H_2] - k_3[H][O_2] + k_4[O][H_2] - k_5[H][O_2][M] - k_6[H] = 0$
- $d[O]/dt = k_3[H][O_2] - k_4[O][H_2] = 0$
- By properly combining these equations one has

$$v(t) = \tfrac{1}{2}d[H_2O]/dt = (k_1[H_2][O_2](k_5[O_2][M]+k_6)/(k_5[H][O_2][M]+k_6-k_3[O_2])$$

THE TRANSITION STATE THEORY

- Assume that the reactant (X) is converted to the product (W) through the intermediate ($X^{\pm}$)
- Assume that the intermediate ($X^{\pm}$) is in Boltzmann equilibrium with X ($K^{\pm}=[X^{\pm}]/[X]=\exp(-\Delta G^{o\pm}_f/_BT)$)
- Express k_f, the rate of the forward process *f*, as $k_f=(k_BT/h)\exp(-\Delta G^{o\pm}_f/k_BT)$
- Thanks to the relantionships between $\Delta G^{o\pm}$, $\Delta H^{o\pm}$ and the activation energy ΔE^{o}_f (see the figure) one can write
- $k_f=(k_BT/h)\exp(-\Delta E^{o}_f/k_BT)$



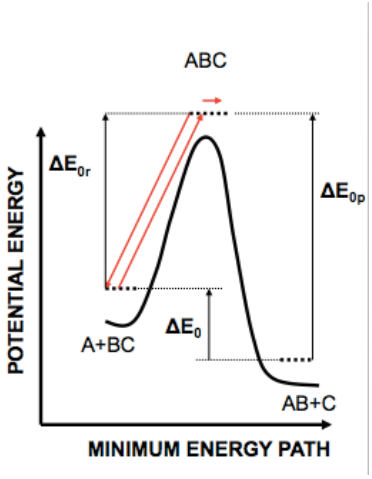
THE A + BC RATE COEFFICIENT k(T)

- The population of the transition state ABC in equilibrium with the reactant A + BC (Q_X is the partition function of X)

$$\frac{Q^{\mp}_{ABC}}{Q_{BC}Q_A}\exp[-E_{0r}/k_BT]$$

- The rate coefficient is given by the frequency of crossing towards products k_BT/h times the above defined population of the transition state

$$k(T)=\frac{vk_BT}{h}\frac{Q^{\mp}_{ABC}}{Q_{BC}Q_A}\exp[-E_{0r}/k_BT]$$



DETAILED STATE TO STATE RATE COEFFICIENTS

- In the collision theory approach the rate coefficient *k(T)* can be expressed as a sum of initial state *i* to final state *f* (detailed) rate coefficients $k_{i,f}(T)$

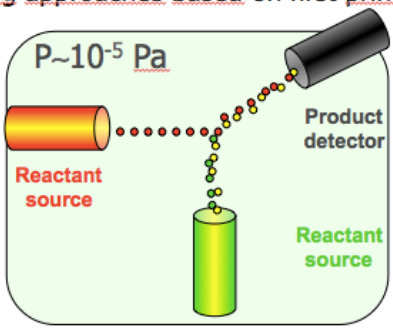
$$k(T)=\sum_i\sum_f\frac{w_ie^{-\varepsilon_i/k_BT}}{Q_{\text{int}}(T)}k_{if}(T)$$

- Then the detailed rate coefficient $k_{i,f}(T)$ can be given in terms of single collision experimental (and theoretical) properties like the state to state cross sections $\sigma_{i,f}(E_{tr})$ depending on collision energy E_{tr}

$$k_{i,f}(T)=\sqrt{\frac{8}{\pi\mu k_B^3T^3}}\int_0^{\infty}E_{tr}\sigma_{i,f}(E_{tr})e^{-E_{tr}/k_BT}dE_{tr}$$

BI-MOLECULAR COLLISIONS

Bi-Molecular (*Molecularity is the number of molecules intervening simultaneously to determine the fate of a molecular process*) single collision (with no chance of undergoing multiple collisions due to the very low pressure of rectant gases) properties can be measured by crossed molecular beams apparatuses. These quantities may also be theoretically and computationally evaluated using approaches based on first principles



CROSSED MOLECULAR BEAMS

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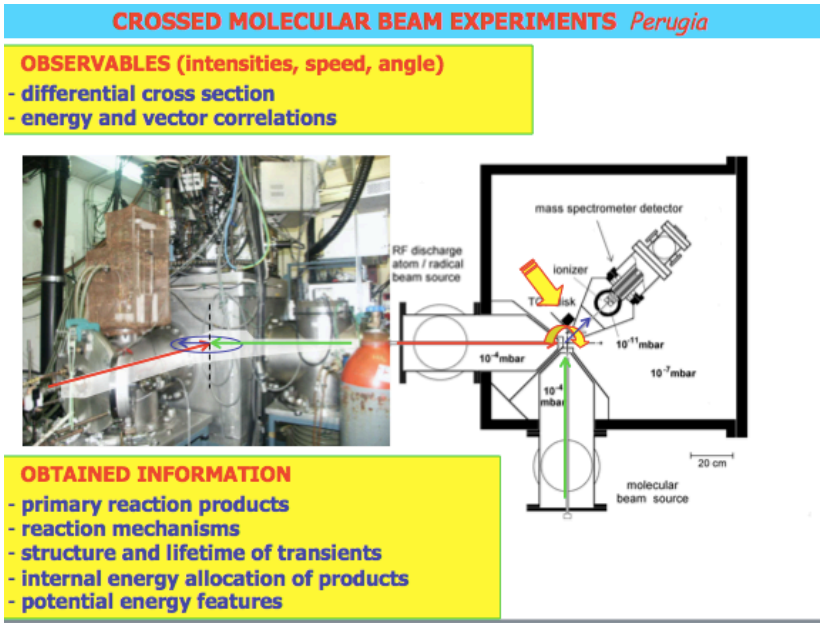

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