

Active Thermochemical Tables: Thermochemistry for the 21st Century

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Office of Science Laboratory
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THANKS TO...

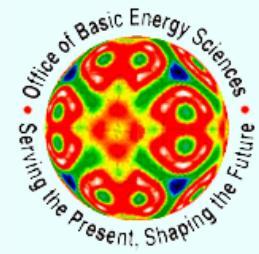
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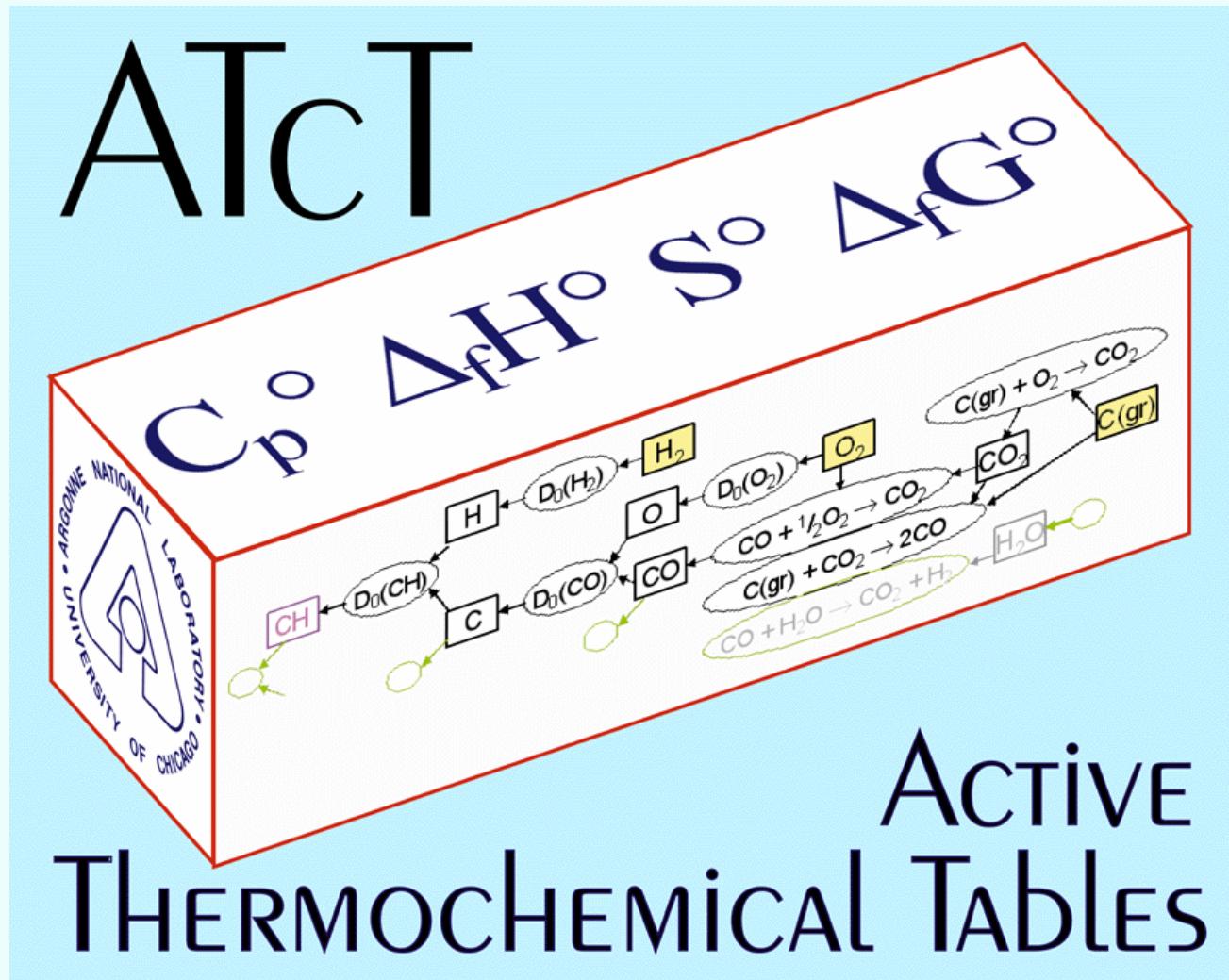
**Division of Mathematical, Information and Computational Sciences,
Office of Advanced Scientific Computing Research**

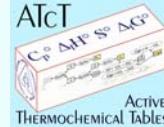


- Numerous collaborators:
 - CMCS Team
 - IUPAC Task Group for Thermochemistry of Radicals
 - Melita L. Morton (ANL/postdoc), Sandra J. Bittner (ANL), Sandeep G. Nijsure (ANL), Michael Minkoff (ANL), Lawrence B. Harding (ANL), Joe V. Michael (ANL), Stephen Gray (ANL), John Stanton (UT Austin), Attila Csaszar (ELTE Budapest), Mihaly Kallay (U. Mainz), Tamas Turanyi (ELTE Budapest), David A. Dixon (U. Ala.), David Feller (PNNL), Kirk Peterson (PNNL/WSU), David Schwenke (NASA Ames), Cheuk-Yiu Ng (UC Davis)...



WHAT ARE ACTIVE THERMOCHEMICAL TABLES?

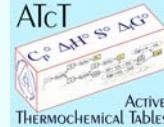




ATcT

WHAT ARE ACTIVE THERMOCHEMICAL TABLES?

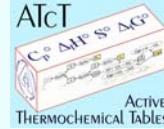
- **Active Thermochemical Tables (ATcT):**
a novel scientific application, centered on a
distinctively different paradigm of how to derive
*accurate, reliable, and internally consistent
thermochemical values*
 - thermochemistry as it befits the 21st century
 - rapidly becoming the archetypal approach
(ATcT are appearing as a new encyclopedic term in the
2005 Yearbook of Science and Technology, an annual update to the
McGraw-Hill Encyclopedia of Science and Technology)
 - first implementation of the broader idea
of **Active Tables**



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WHAT IS THE GENERAL IDEA BEHIND ACTIVE TABLES?

- Many databases store and display data items that:
 - are *not directly measurable observables*, and
 - are *interdependent* in a non-transparent way, because they are
 - *derived* in a (usually) complex way from *more basic determinations*
- In most cases, these databases ***do not expose or even store*** either
 - the basic determinations, or
 - the data interdependencies
- Dear consequence:
 - the database cannot be easily updated when new information becomes available and hence becomes obsolete
- The idea behind ***Active Tables*** is not to store derived data, but rather ***the basic determinations and the dependencies***, and ***update the derived data as frequently as needed***

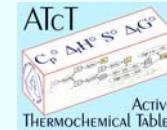


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WHAT DO WE NEED GOOD THERMOCHEMISTRY FOR?

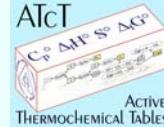
- Knowledge of thermochemical stability of chemical species is central to chemistry and essential in many industries
- Accurate, reliable, and self-consistent thermochemistry is
 - a *conditio sine qua non* in chemical kinetics, construction of reaction mechanisms, formulation of multi-scale chemical models that have predictive abilities, etc.
 - historically the strongest spiritus movens for the development and improvement of electronic structure theories
 - a stimulating environment fostering abstraction of generalities leading to new insights into details of chemical bonding
- Availability of well-defined and properly quantified uncertainties is becoming increasingly important as the fidelity levels of electronic structure theory and computer modeling of complex chemical environments are increasing

THERMOCHEMICAL TABLES



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- Tabulations of thermochemical properties, conveniently sorted by chemical species
- Tabulated thermochemical properties are derived from other, more direct determinations
 - **Species-interrelating** determinations
(D_0 , $\Delta_f H^\circ_T$, K°_{eqT} , electrode potentials, solub. const's, etc)
→ $\Delta_f H^\circ$ and/or $\Delta_f G^\circ$ at one temperature
 - **Species-specific** determinations
(lists of levels, spectroscopic constants, direct measurements of C_p , etc)
→ partition-function Q_T related thermochemical info:
 $[H^\circ_T - H^\circ_0]/RT = T \partial(\ln Q_T)/\partial T = <E>/kT = \int C^\circ_{pT}/R dT$
 $S^\circ_T/R = T \partial(\ln Q_T)/\partial T + \ln Q_T = <E>/kT + \ln Q_T = \int C^\circ_{pT}/R/T dT$
 $\Phi^\circ_T/R = \ln Q_T = S^\circ_T/R - [H^\circ_T - H^\circ_0]/RT$
 $C^\circ_{pT}/R = T^2 \partial^2(\ln Q_T)/\partial T^2 + 2 T \partial(\ln Q_T)/\partial T = <E^2>/(kT)^2 - (<E>/kT)^2$
and T-dependence of $\Delta_f H^\circ$ and $\Delta_f G^\circ$



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TRADITIONAL SEQUENTIAL THERMOCHEMISTRY

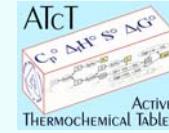
- The nature of the inexorable **species-interrelating determinations** causes considerable complications...
- Traditional approach: **sequential thermochemistry**
 - one target species per step
 - available **species-interrelating** information relating the target species *to those previously determined* is examined
 - the “**best**” determination is selected manually and used to derive $\Delta_f H^\circ$ at one T
 - available **species-specific** info is used to derive T-dependence and other functions
 - **thermochemistry for the target species is frozen** and used as a constant in subsequent steps
 - sequence follows the “**standard order of the elements**”



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DEFICIENCIES OF THE TRADITIONAL APPROACH

- Traditional thermochemical tables have a maze of *hidden* progenitor-progeny relationships
 - Consequently, traditional tables are next to impossible to properly update with new knowledge
 - New determinations can be used, at best, to “improve” things *locally*, for one target species
 - This immediately introduces *new inconsistencies* across the table, since there will be other species pegged to the old value of the newly revised species; it is not explicit which those may be
- The “adopt and freeze” sequential approach
 - creates a *hidden cumulative error* (lack of feedback to frozen values)
 - produces *uncertainties* that do not properly reflect all the knowledge that was available (e.g. knowledge used only during later steps, or was discarded because it lagged behind the selected “best” determination) (*BTW, uncertainties are the NBT*)
- Available knowledge is used only partially, at best



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THE APPROACH OF ACTIVE THERMOCHEMICAL TABLES

- As opposed to conventional sequential thermochemistry, **Active Thermochemical Tables** are based on the **Thermochemical Network approach**, hence:
 - addressing and correcting the mentioned deficiencies of traditional tables, and, at the same time
 - introducing a number of completely new features (such as: rapid update with new information, “what if” tests, “weakest link” isolation, availability of the full covariance matrix, the sensitivity matrix, etc.)

WHAT IS A THERMOCHEMICAL NETWORK ?



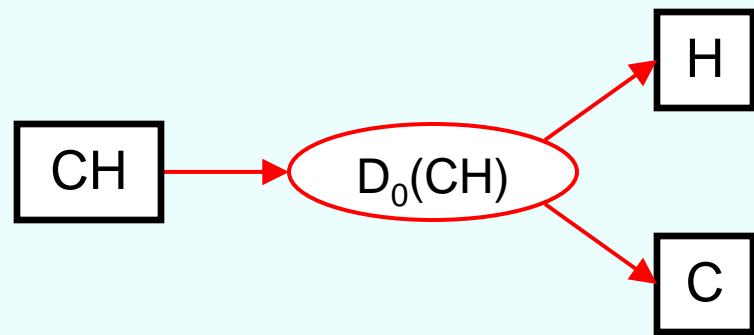
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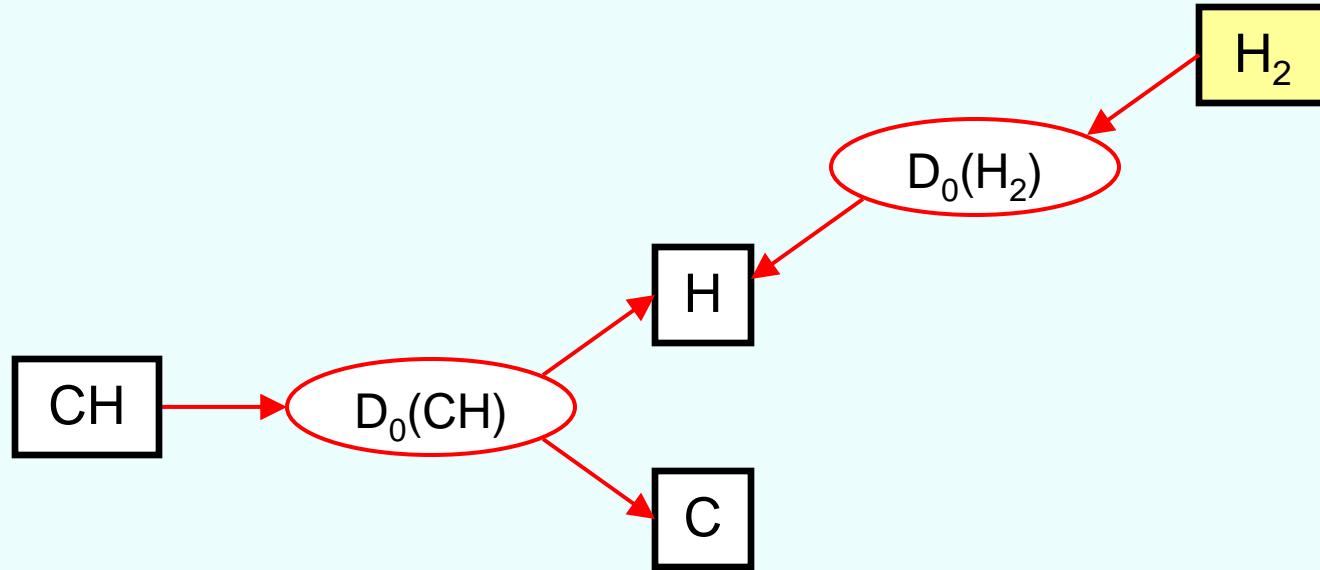
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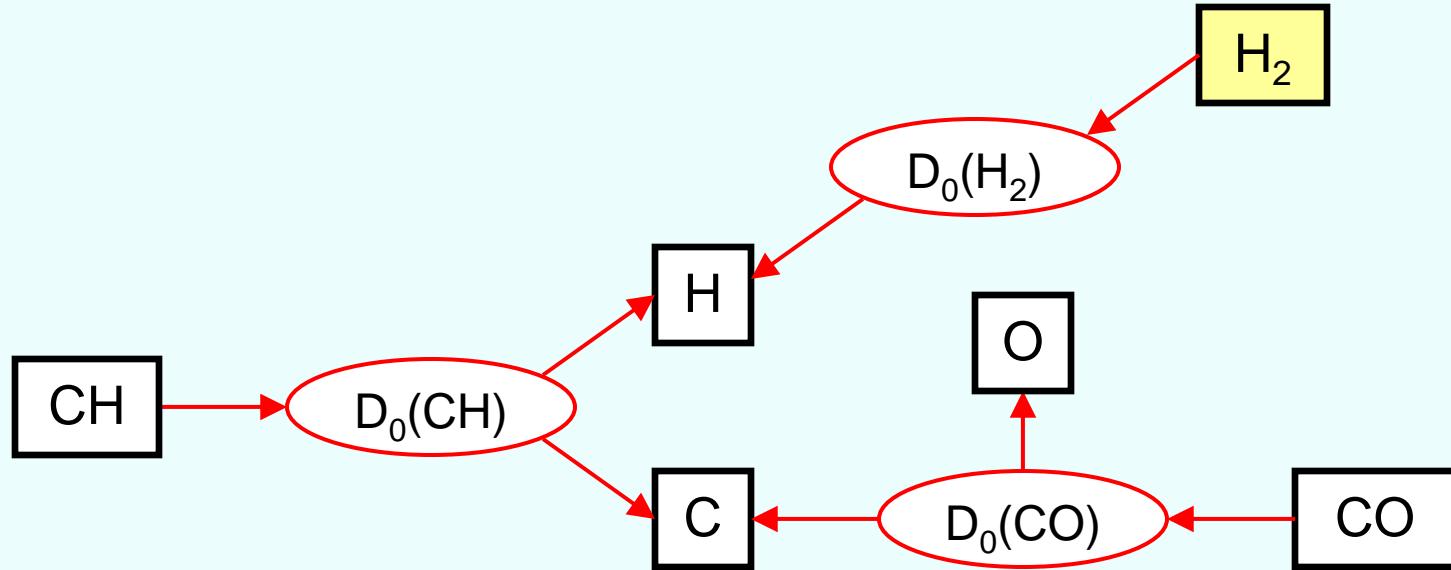
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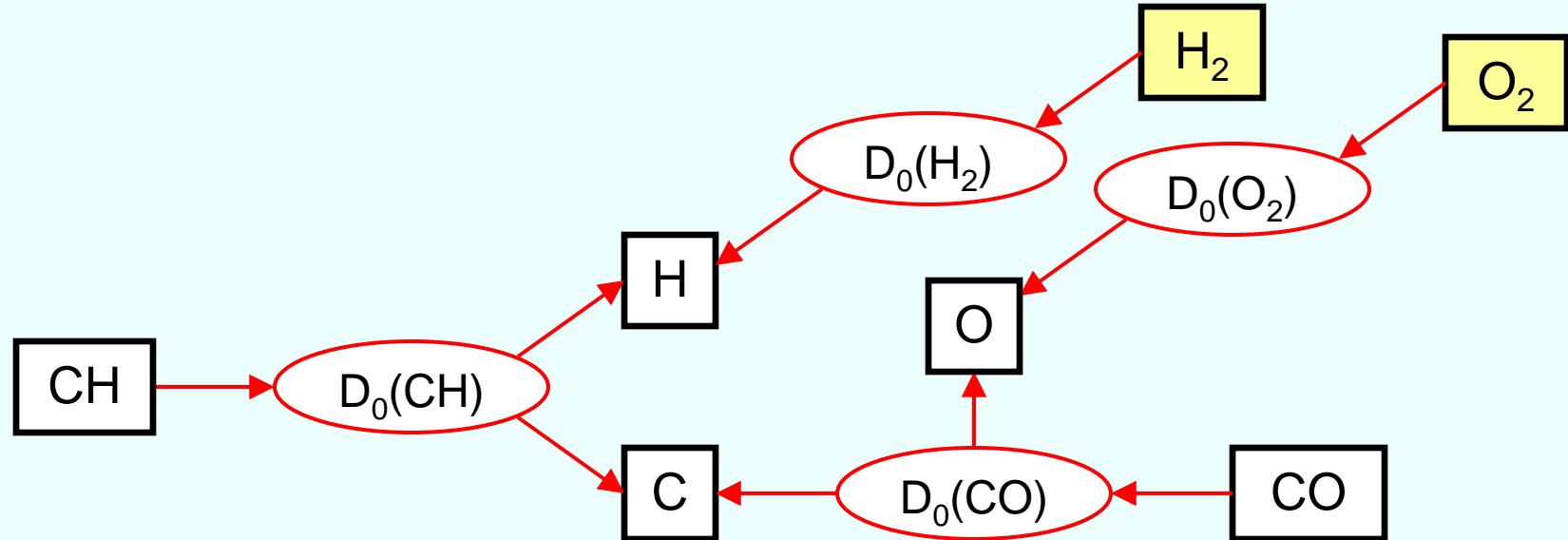
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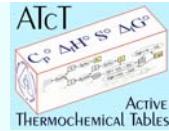
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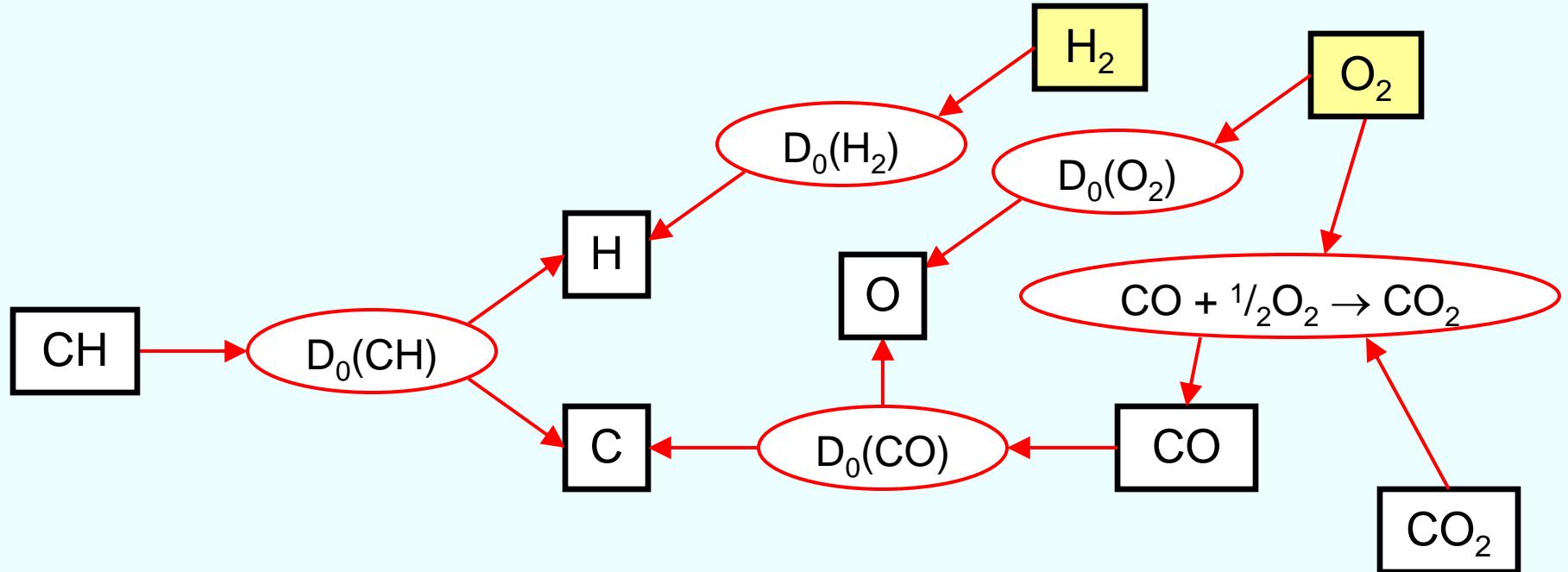
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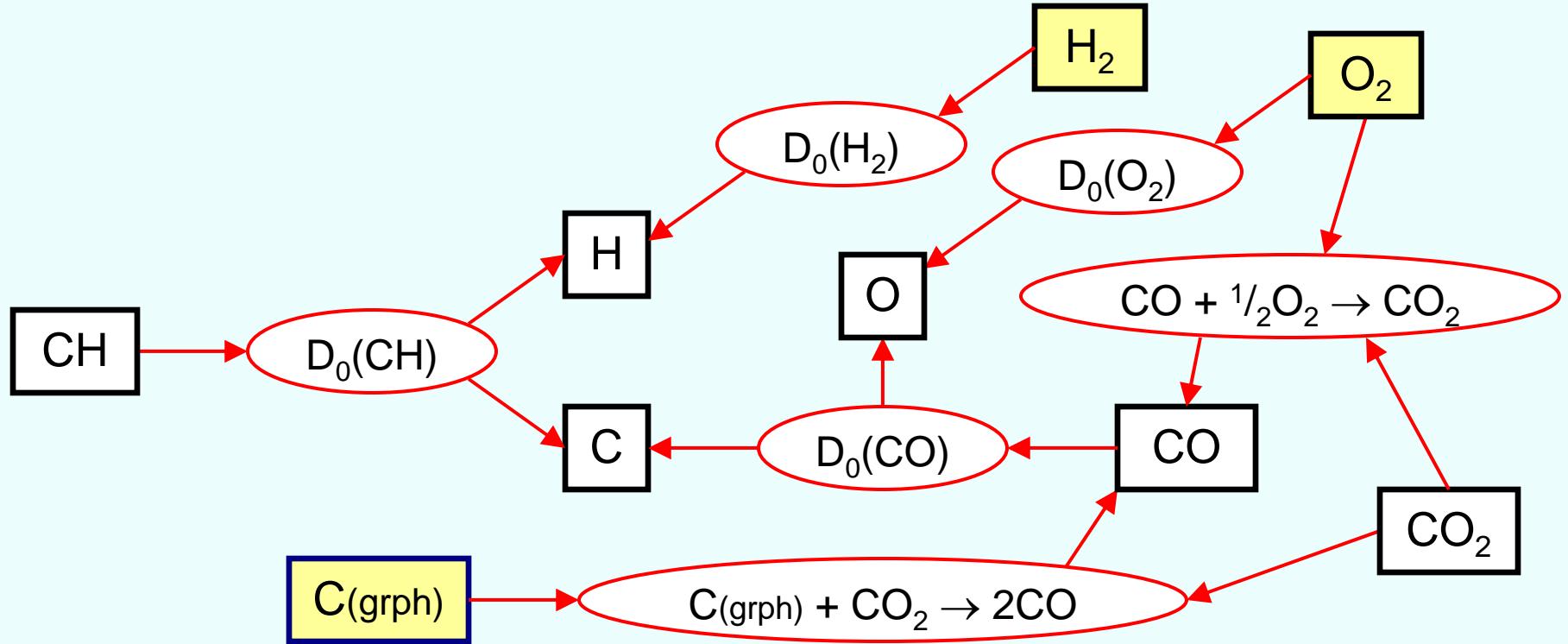
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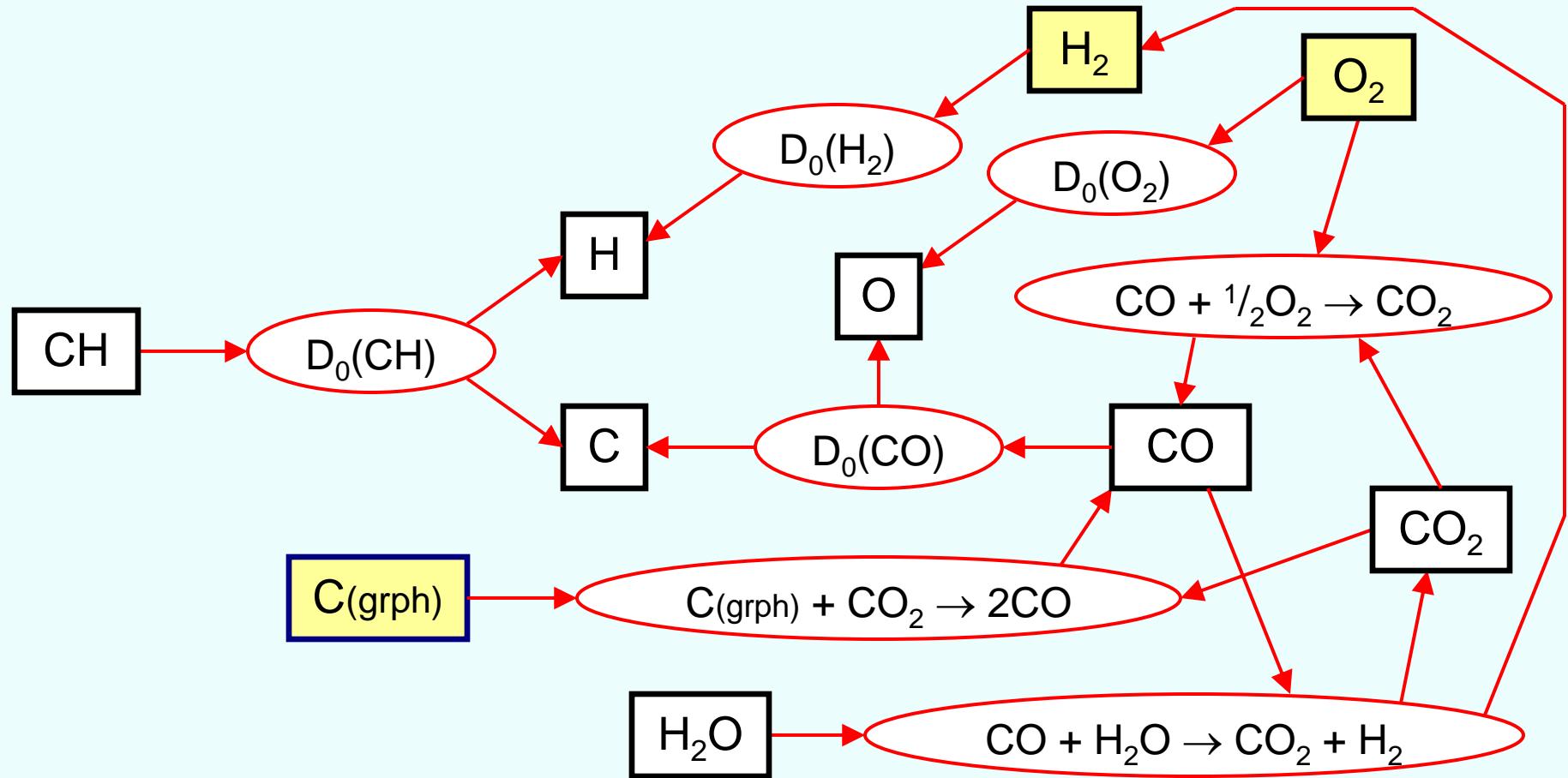
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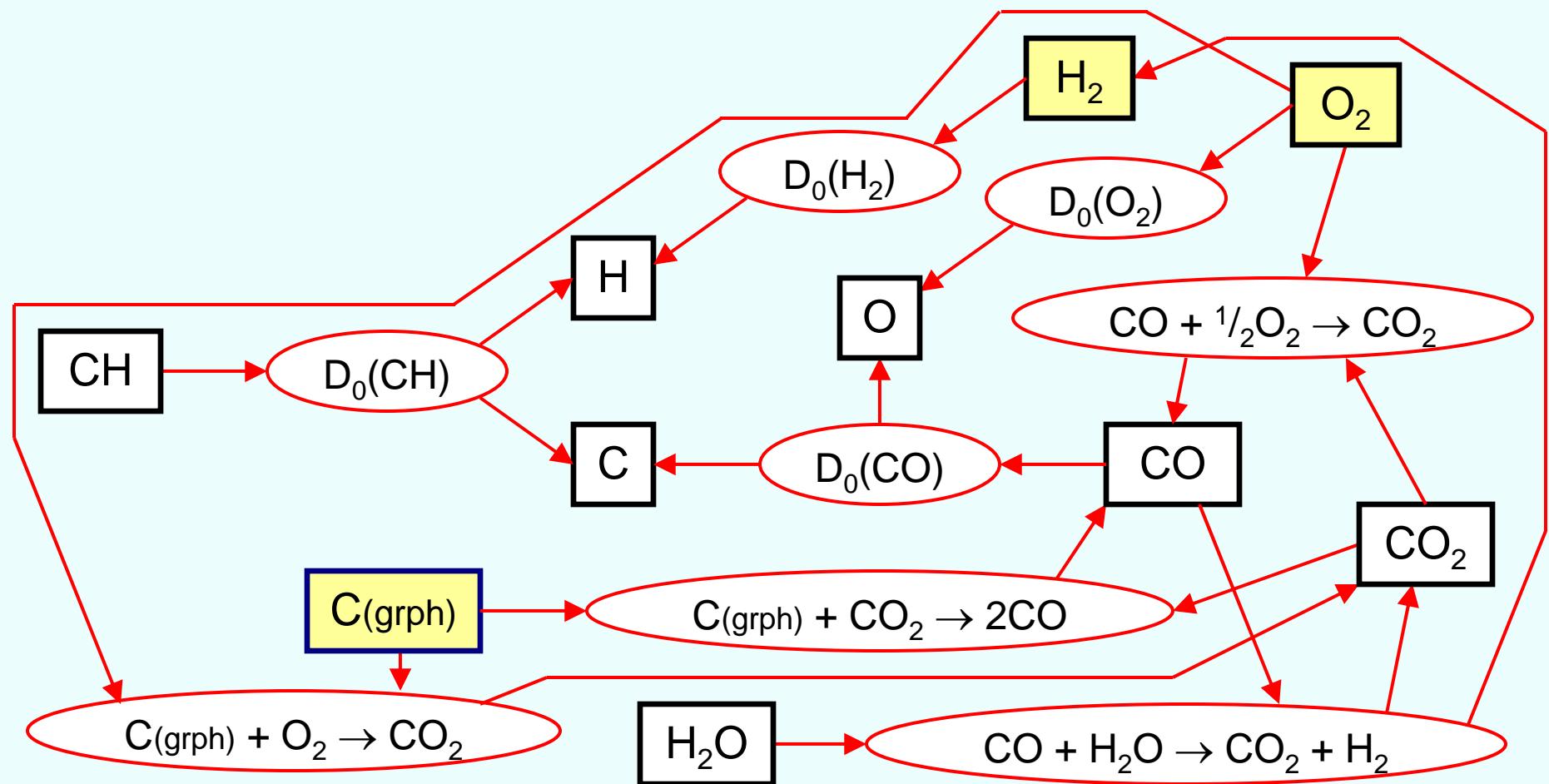
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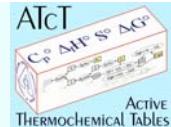
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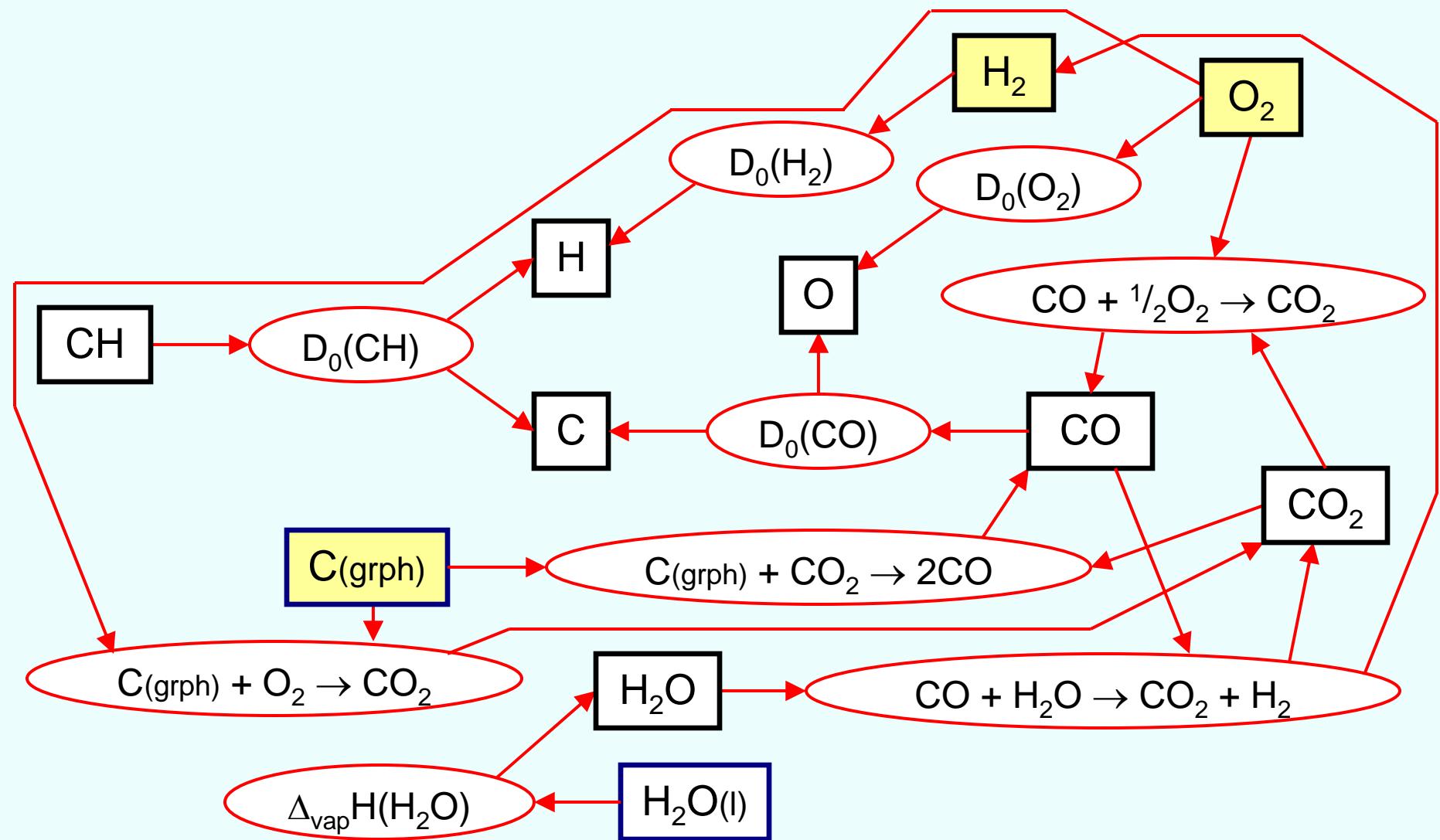
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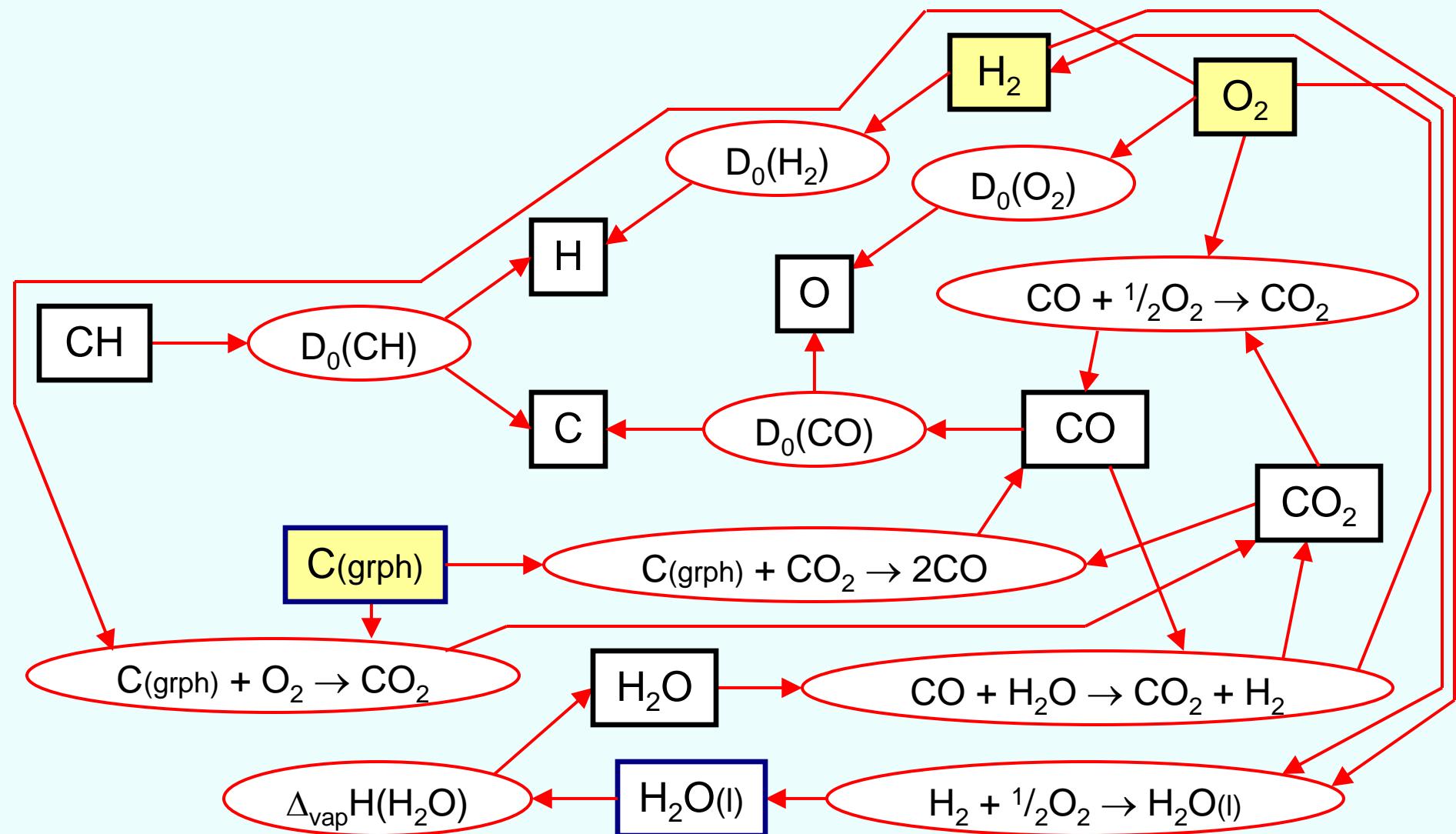
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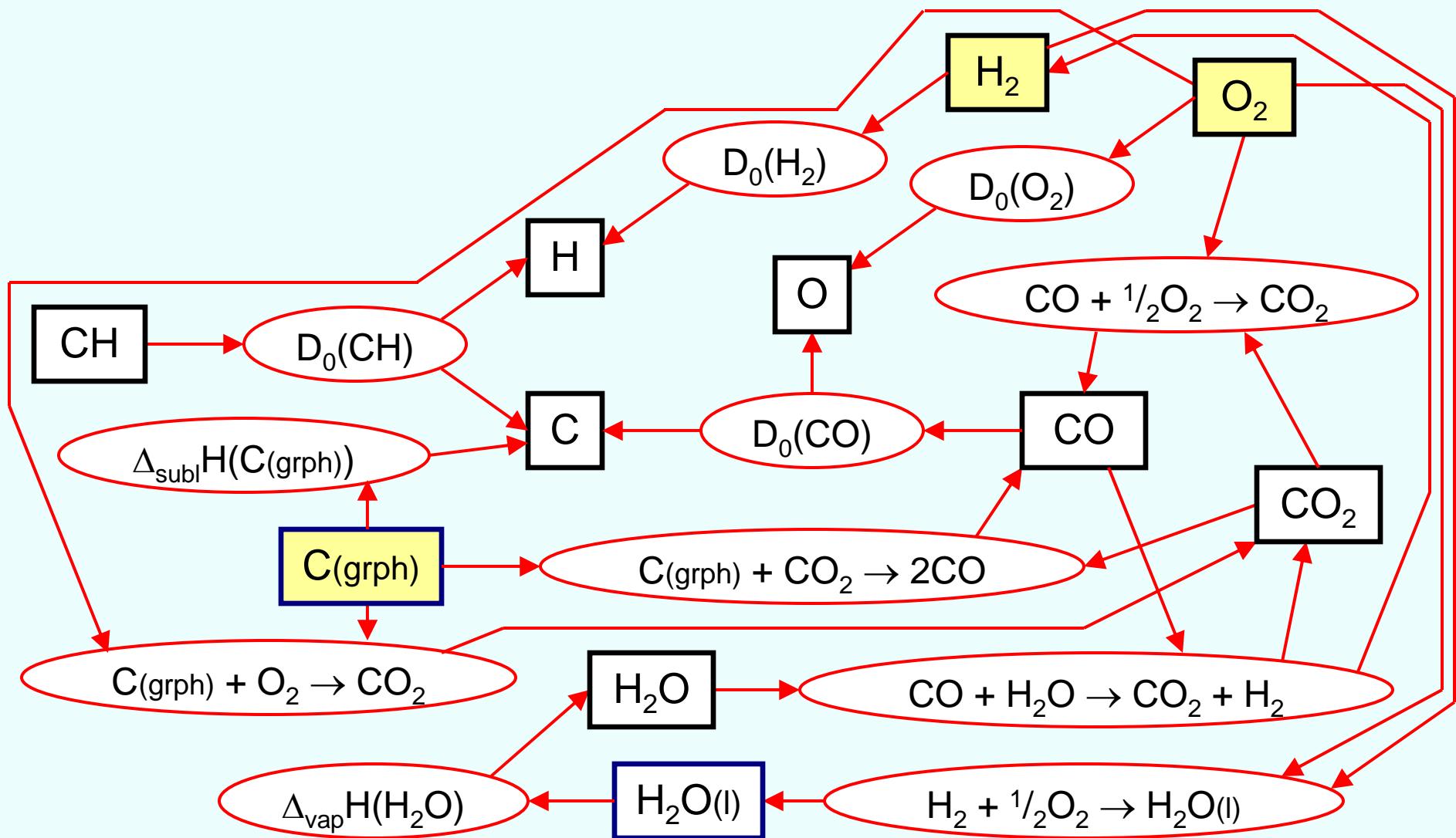
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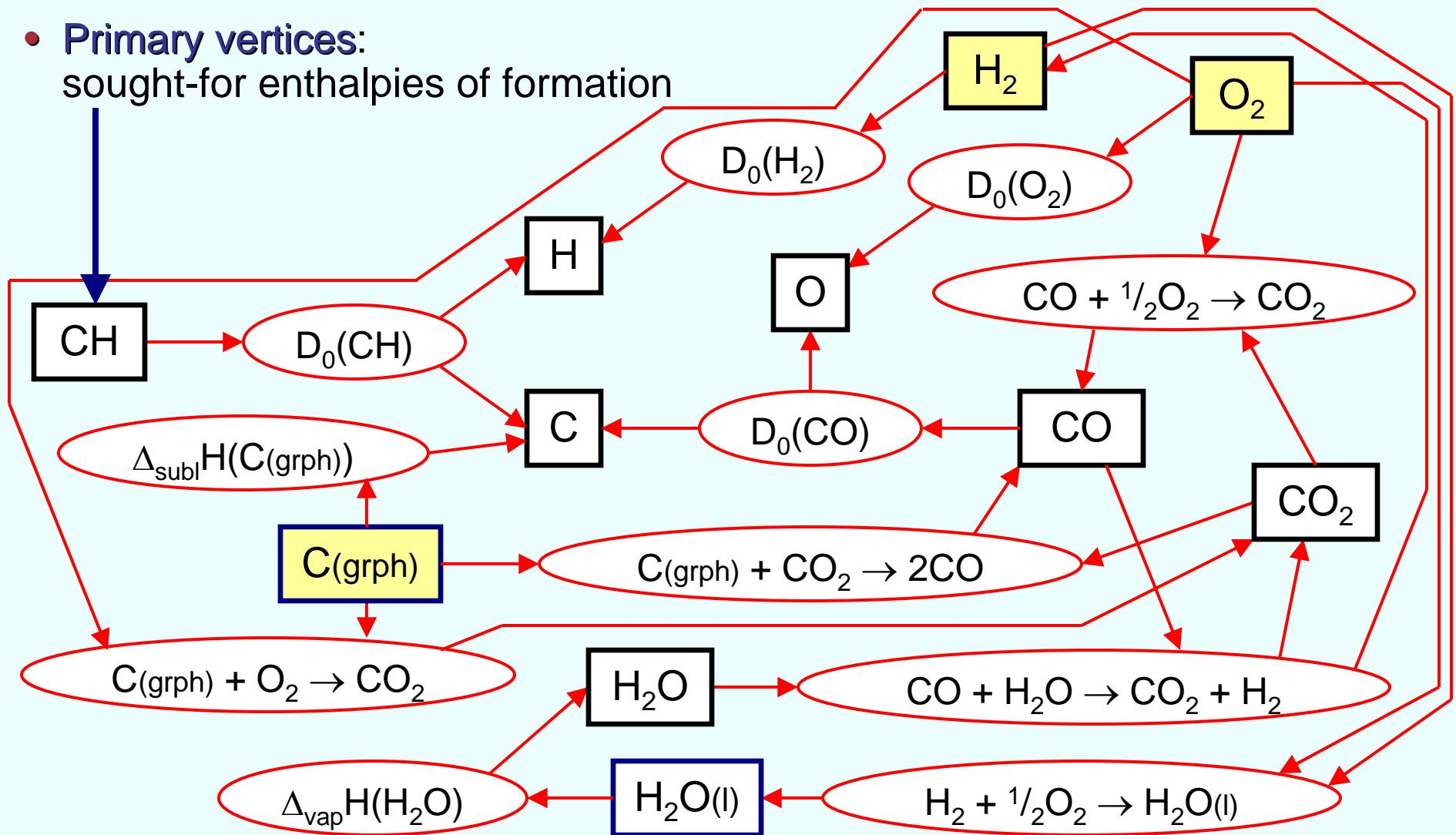
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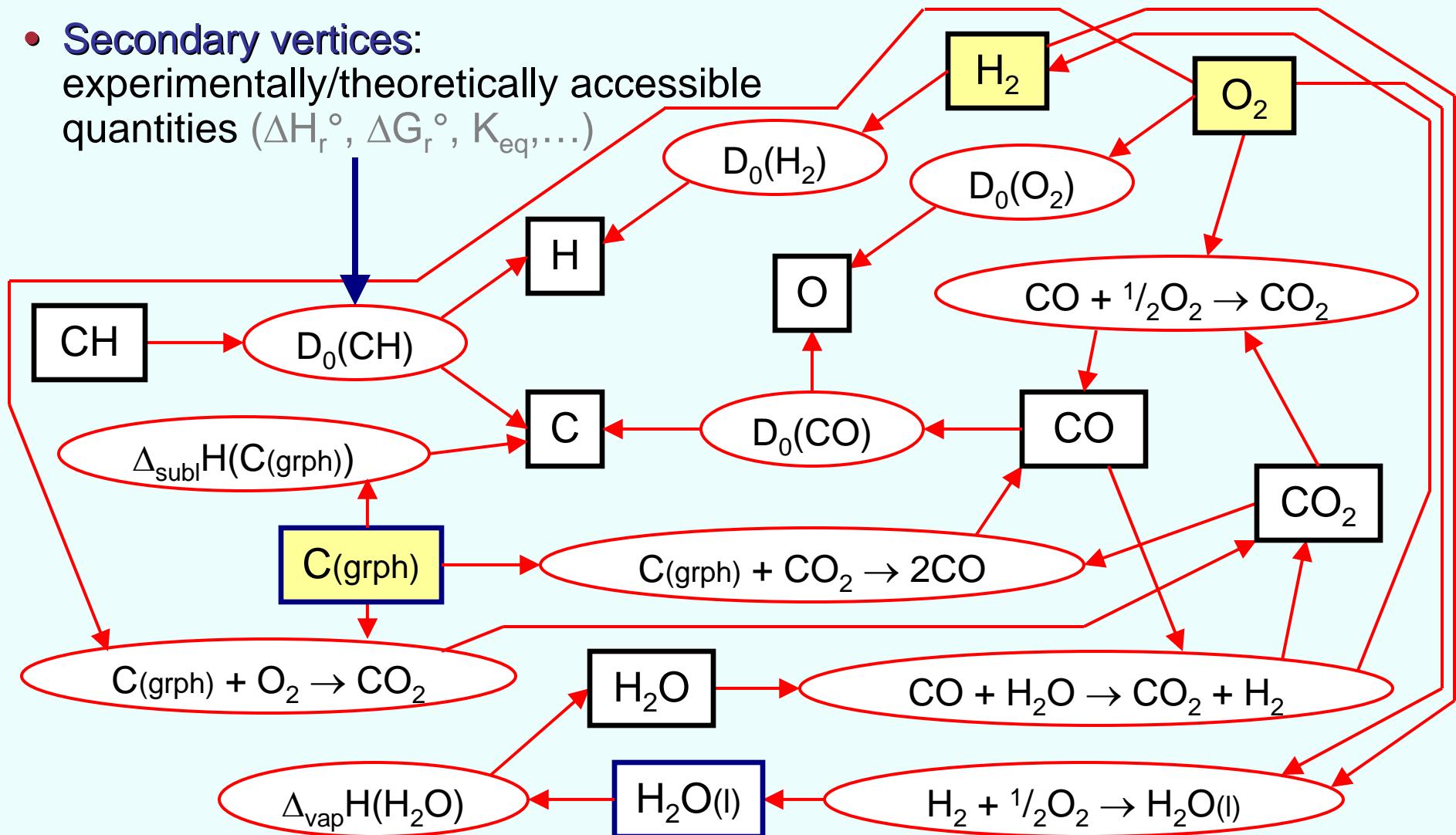


- **Primary vertices:**
sought-for enthalpies of formation

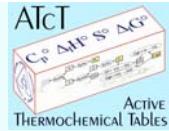


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- **Secondary vertices:**
experimentally/theoretically accessible
quantities (ΔH_r° , ΔG_r° , K_{eq} , ...)

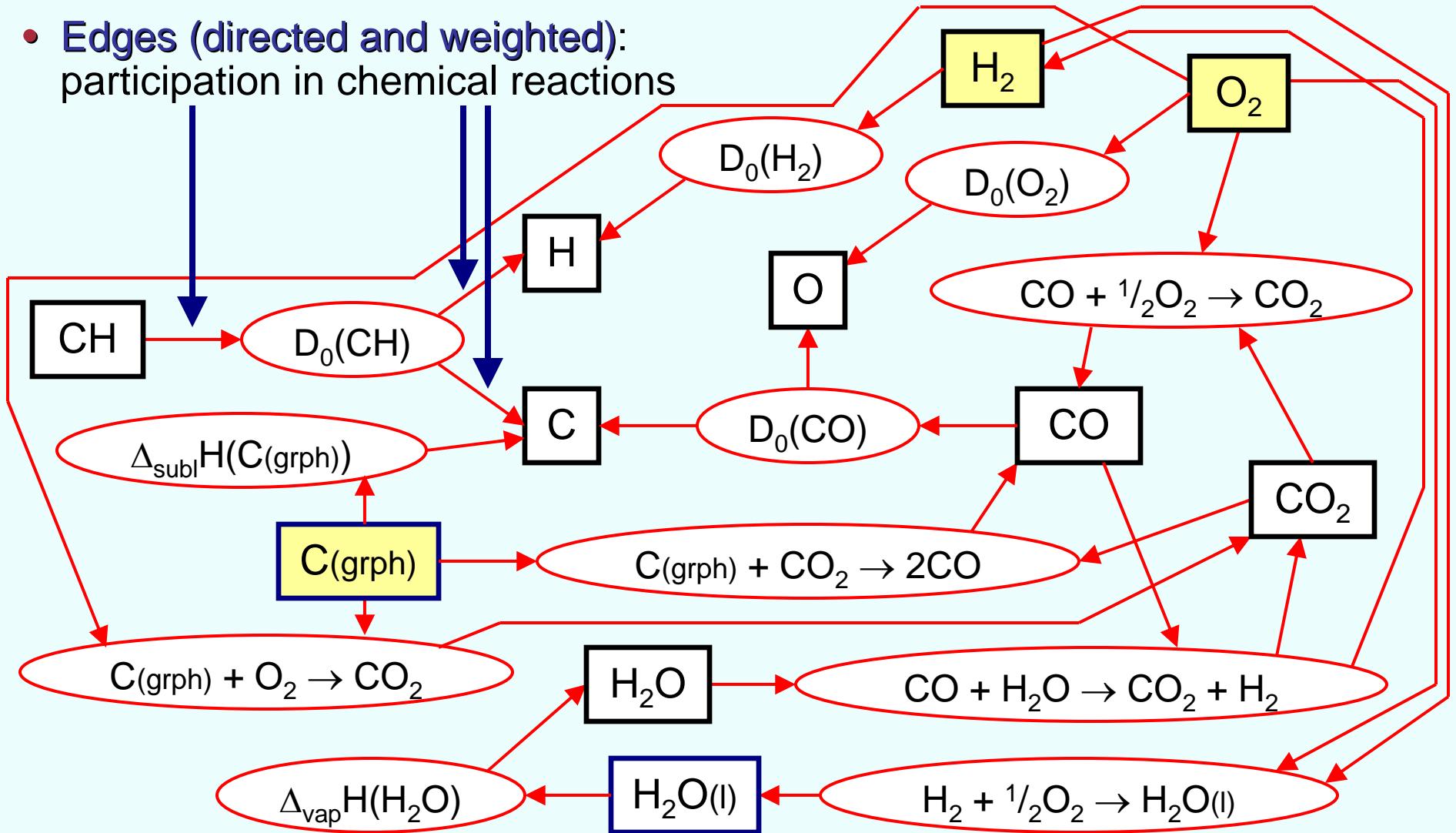


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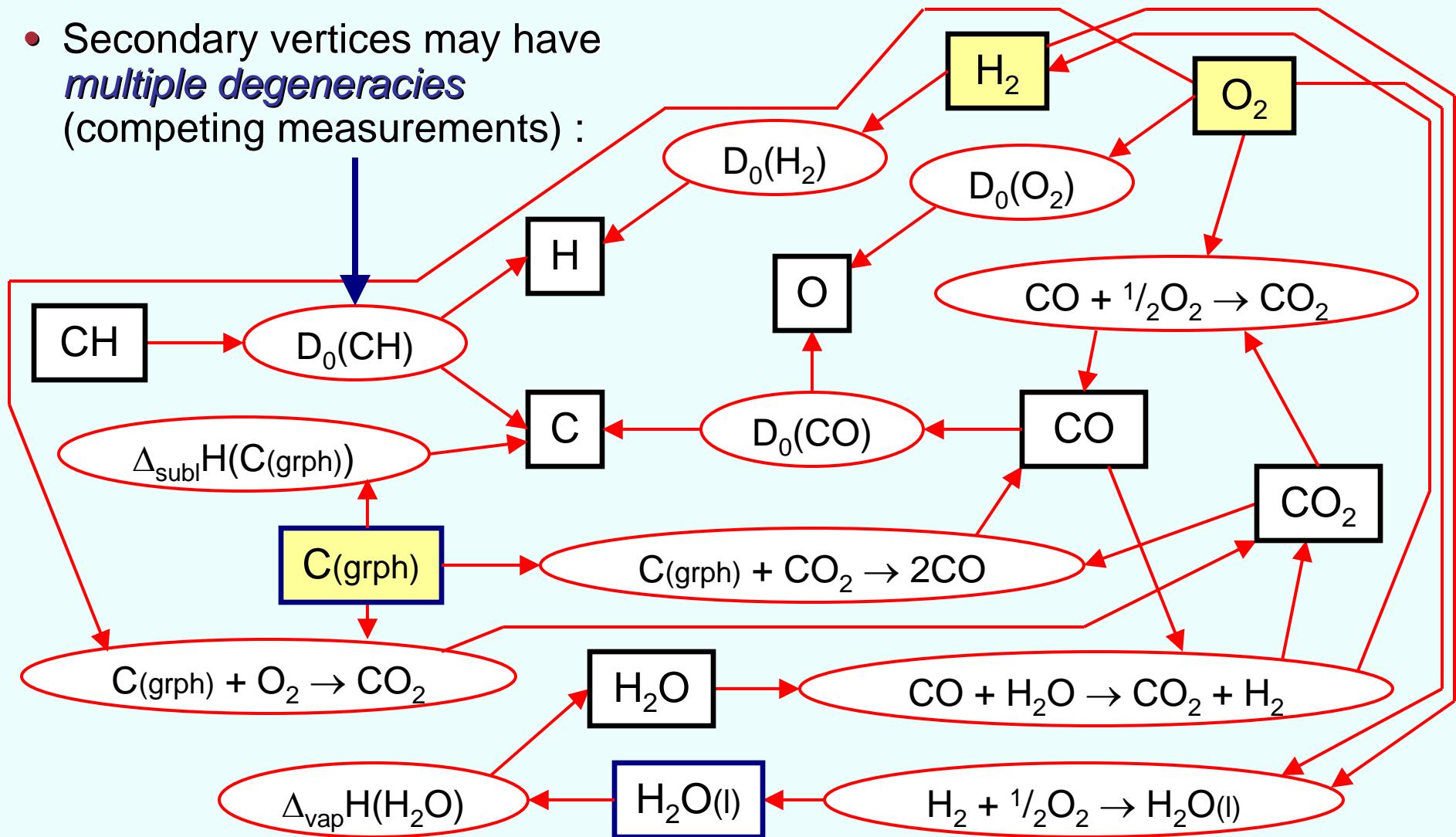
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- **Edges (directed and weighted):** participation in chemical reactions

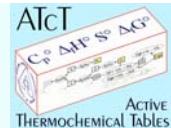


WHAT IS A THERMOCHEMICAL NETWORK ?

- Secondary vertices may have *multiple degeneracies* (competing measurements) :

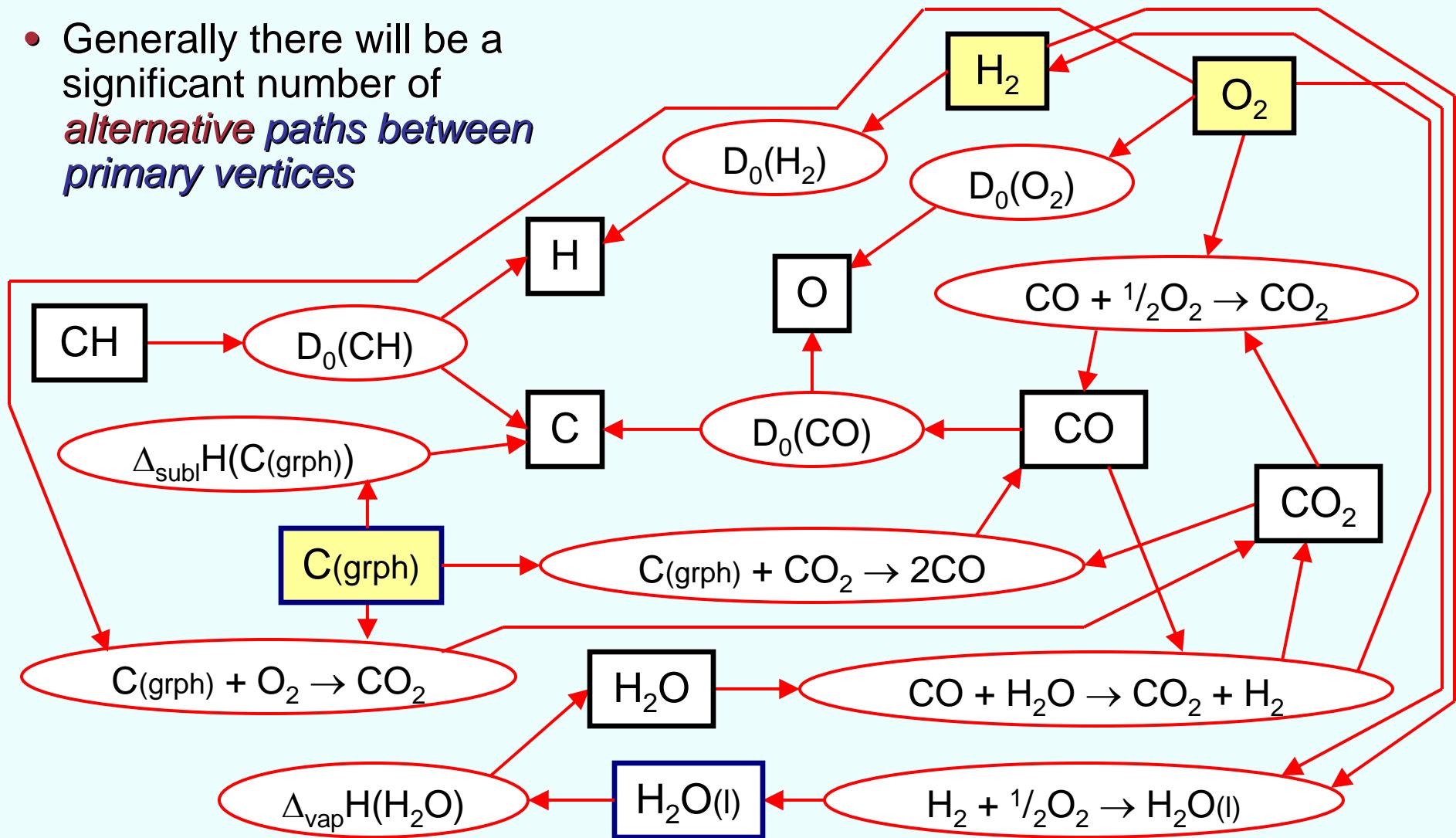


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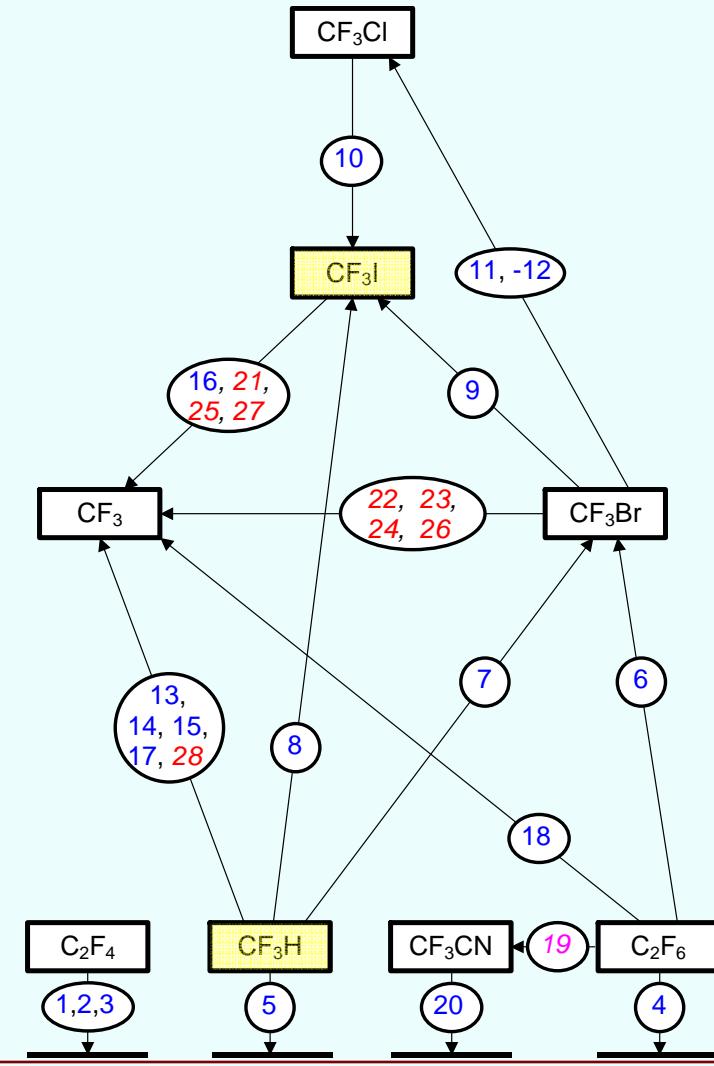


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- Generally there will be a significant number of *alternative paths between primary vertices*

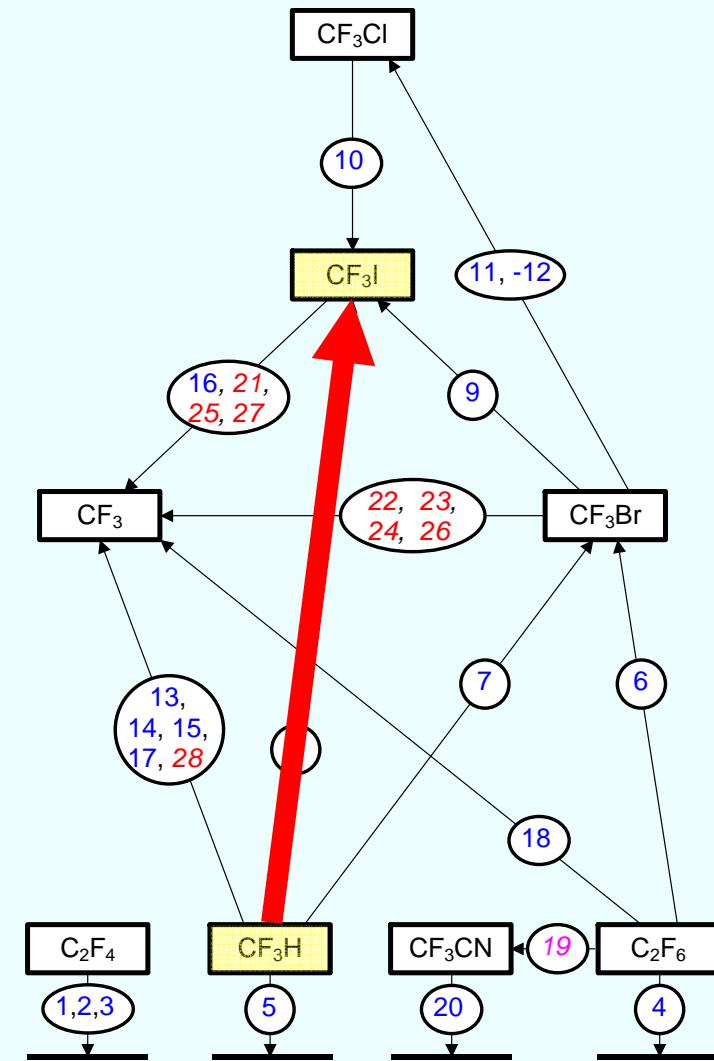


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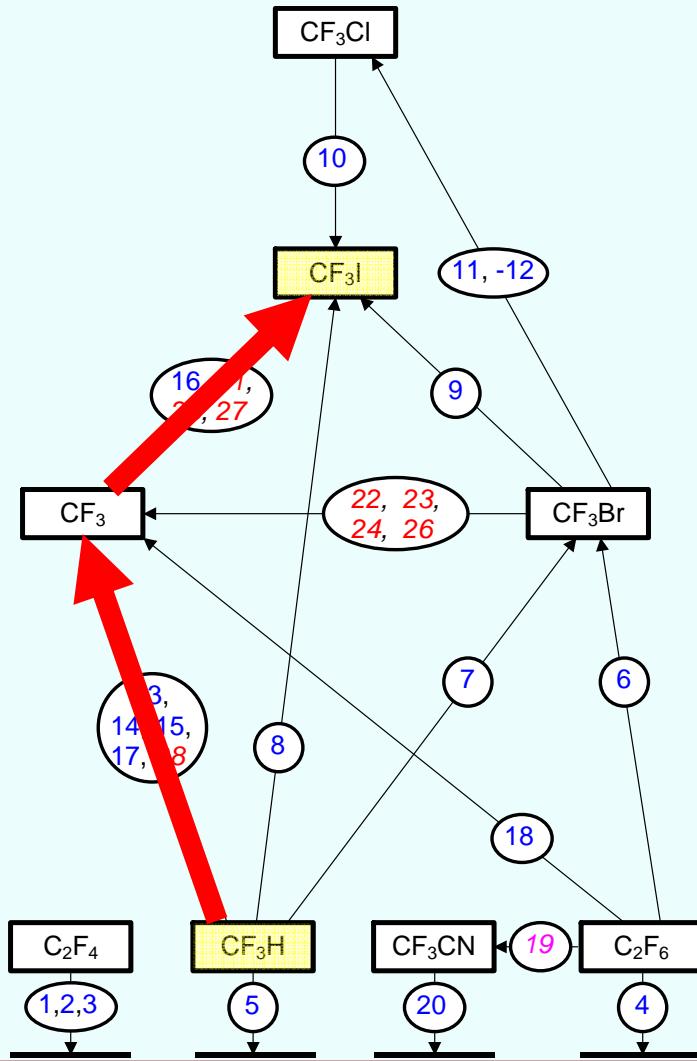
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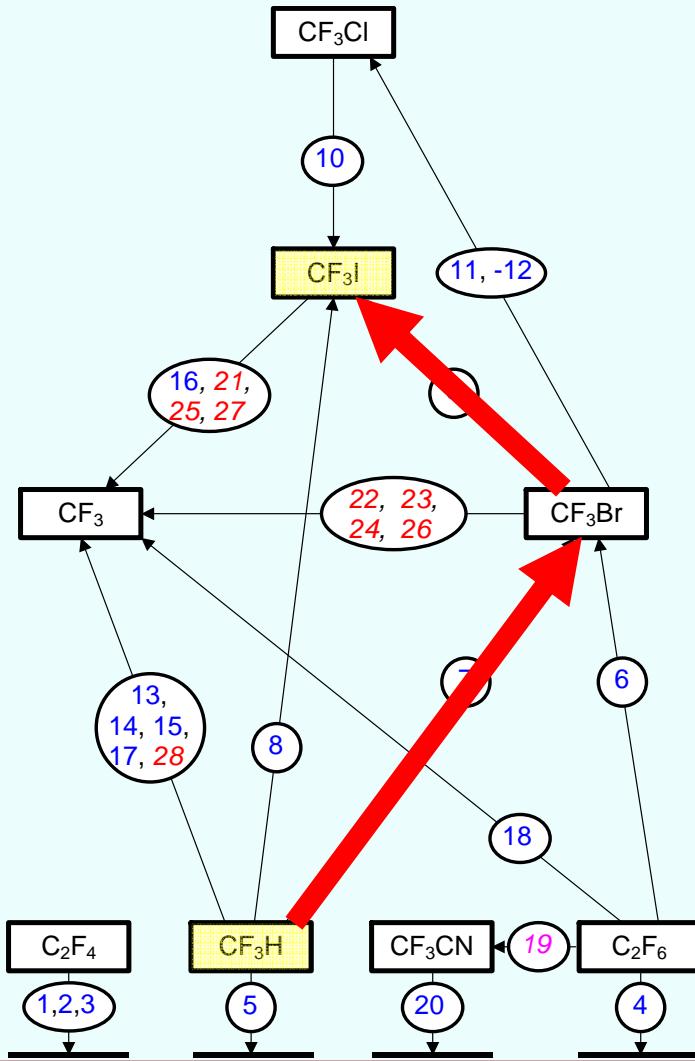
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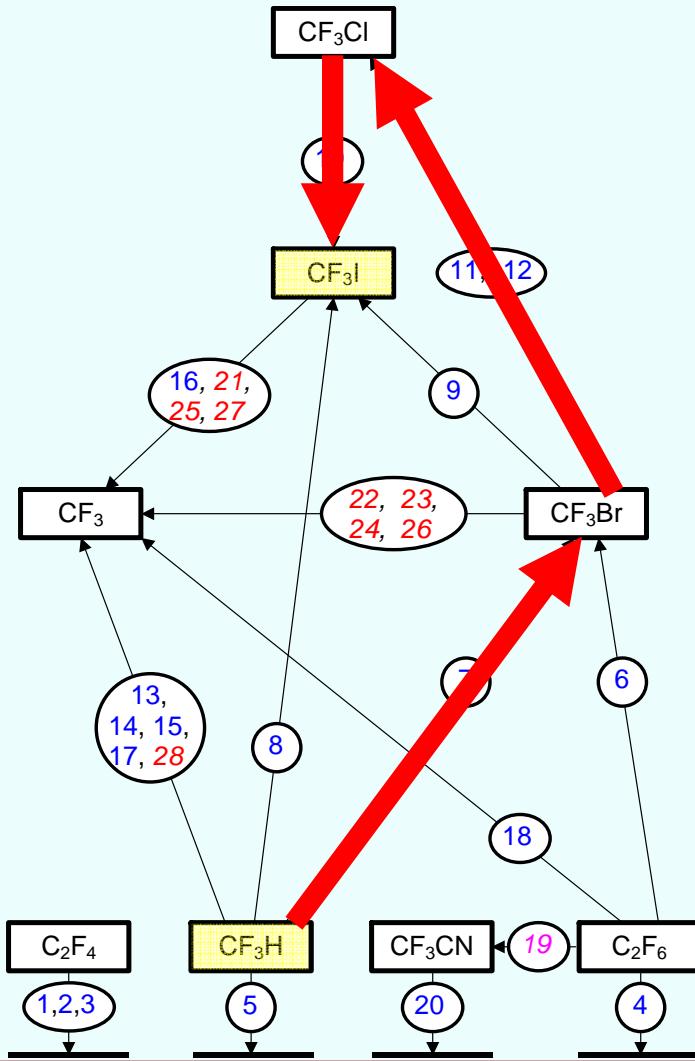
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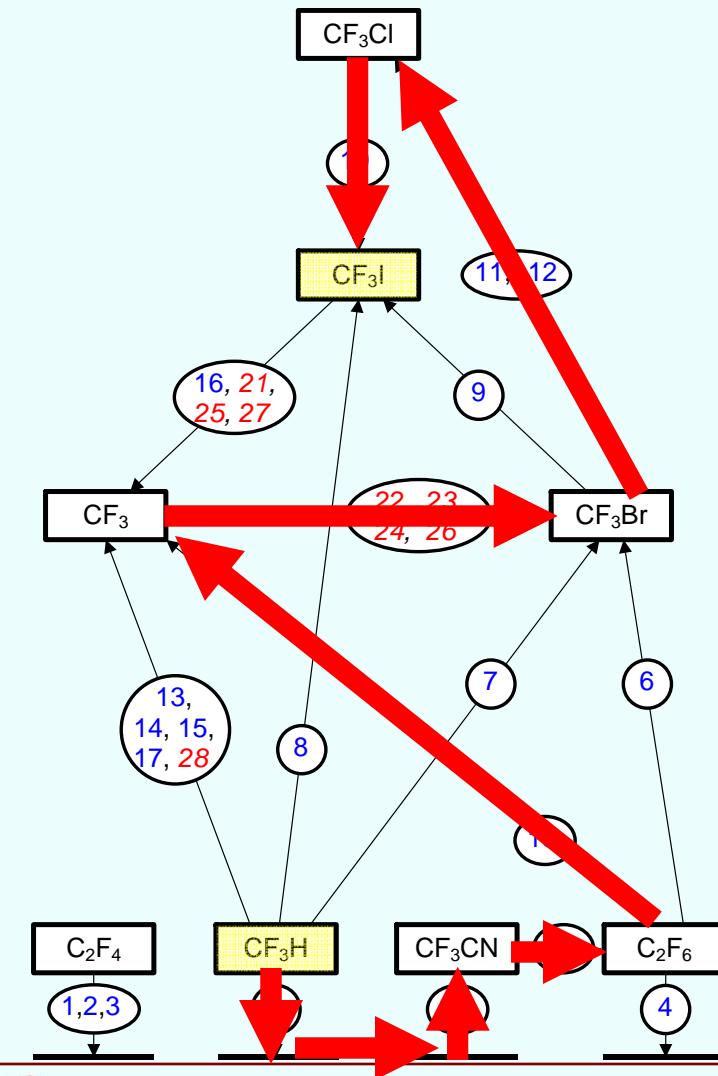
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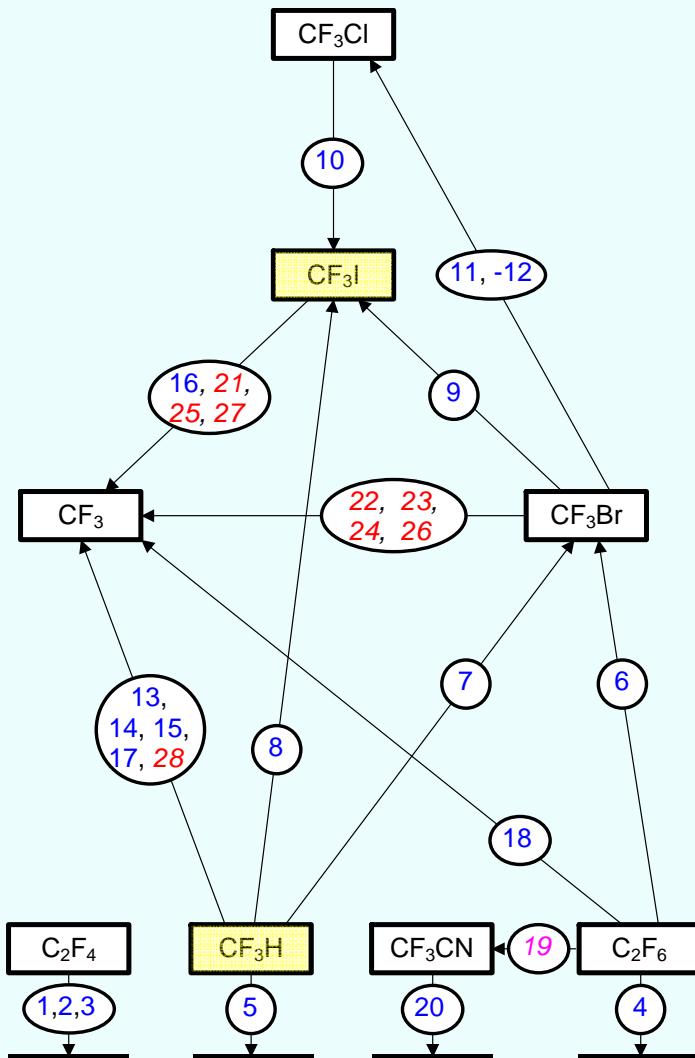
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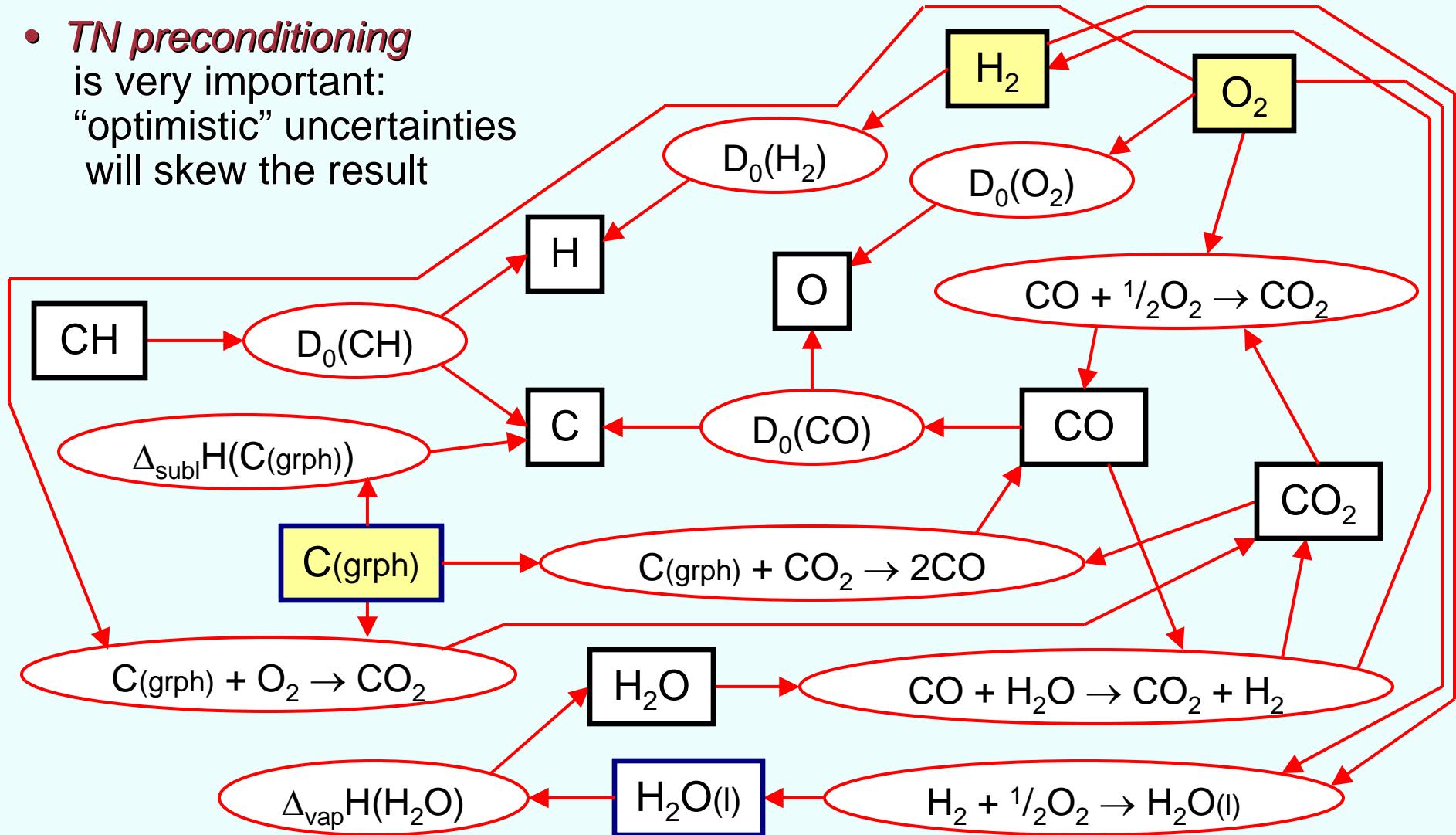
- Generally there will be a significant number of *alternative paths between primary vertices*
- The *best set* of ΔH_f° 's describing *all* underlying knowledge is obtained ~~NOT by choosing a particular sequential path through the TN~~ but by *simultaneous solution* of the network (via minimization of a suitable statistic, such as χ^2), preceded by a *statistical analysis* of TN (to isolate “optimistic” uncertainties)

SOLVING THE THERMOCHEMICAL NETWORK



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- **TN preconditioning** is very important:
“optimistic” uncertainties will skew the result

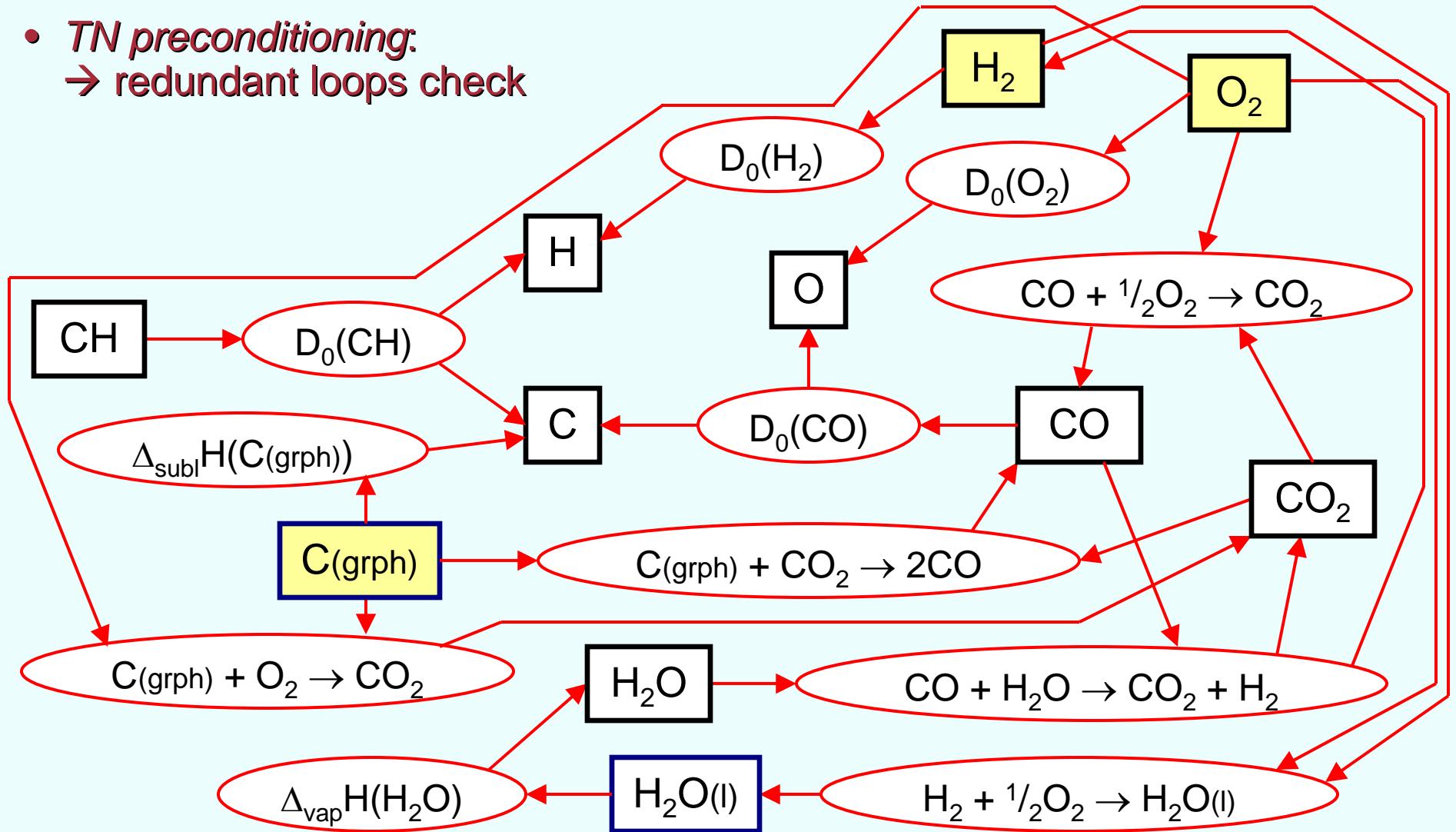


SOLVING THE THERMOCHEMICAL NETWORK



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- *TN preconditioning:*
→ redundant loops check

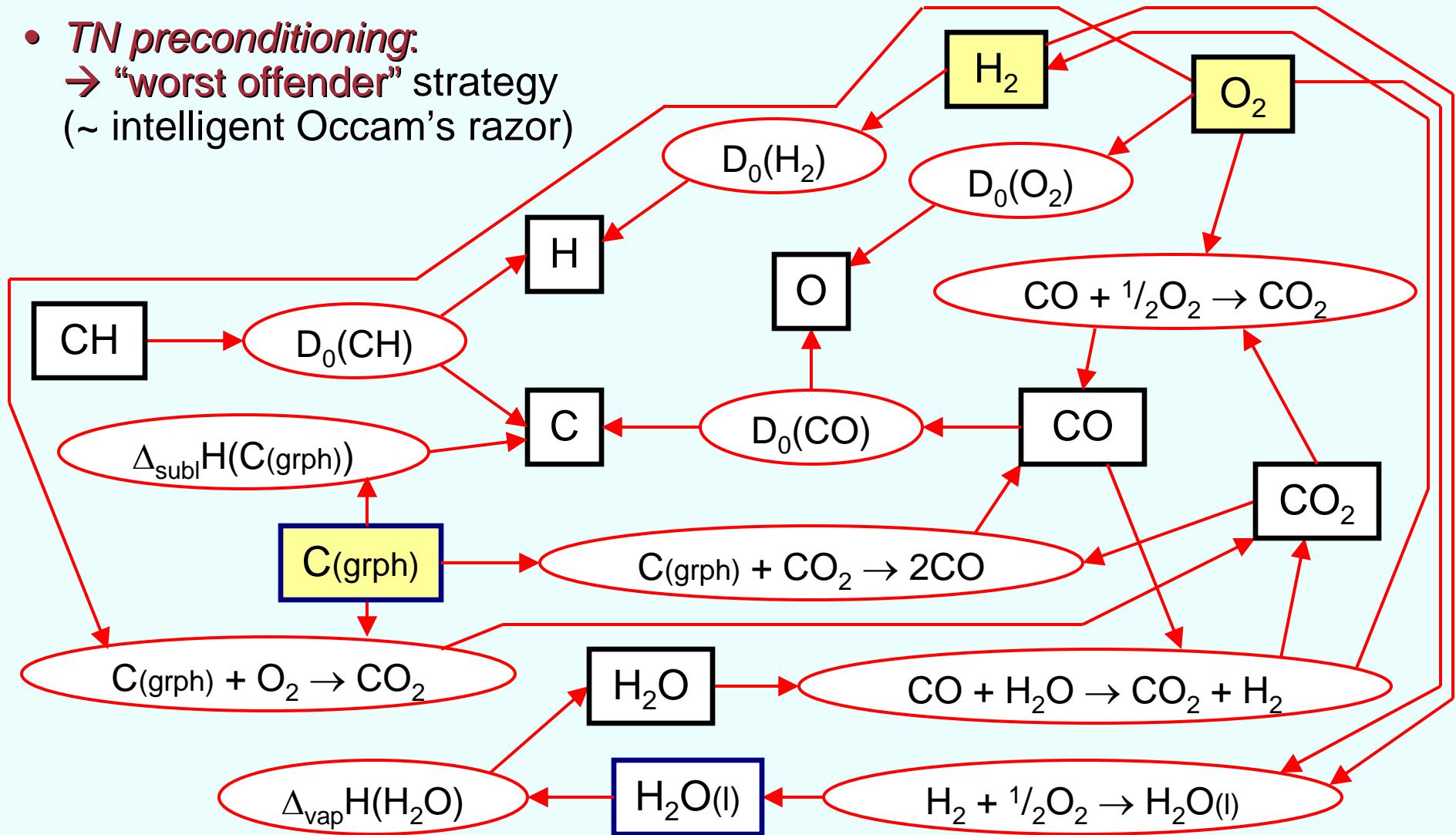


SOLVING THE THERMOCHEMICAL NETWORK

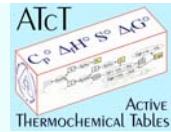


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- **TN preconditioning:**
→ “worst offender” strategy
(~ intelligent Occam’s razor)

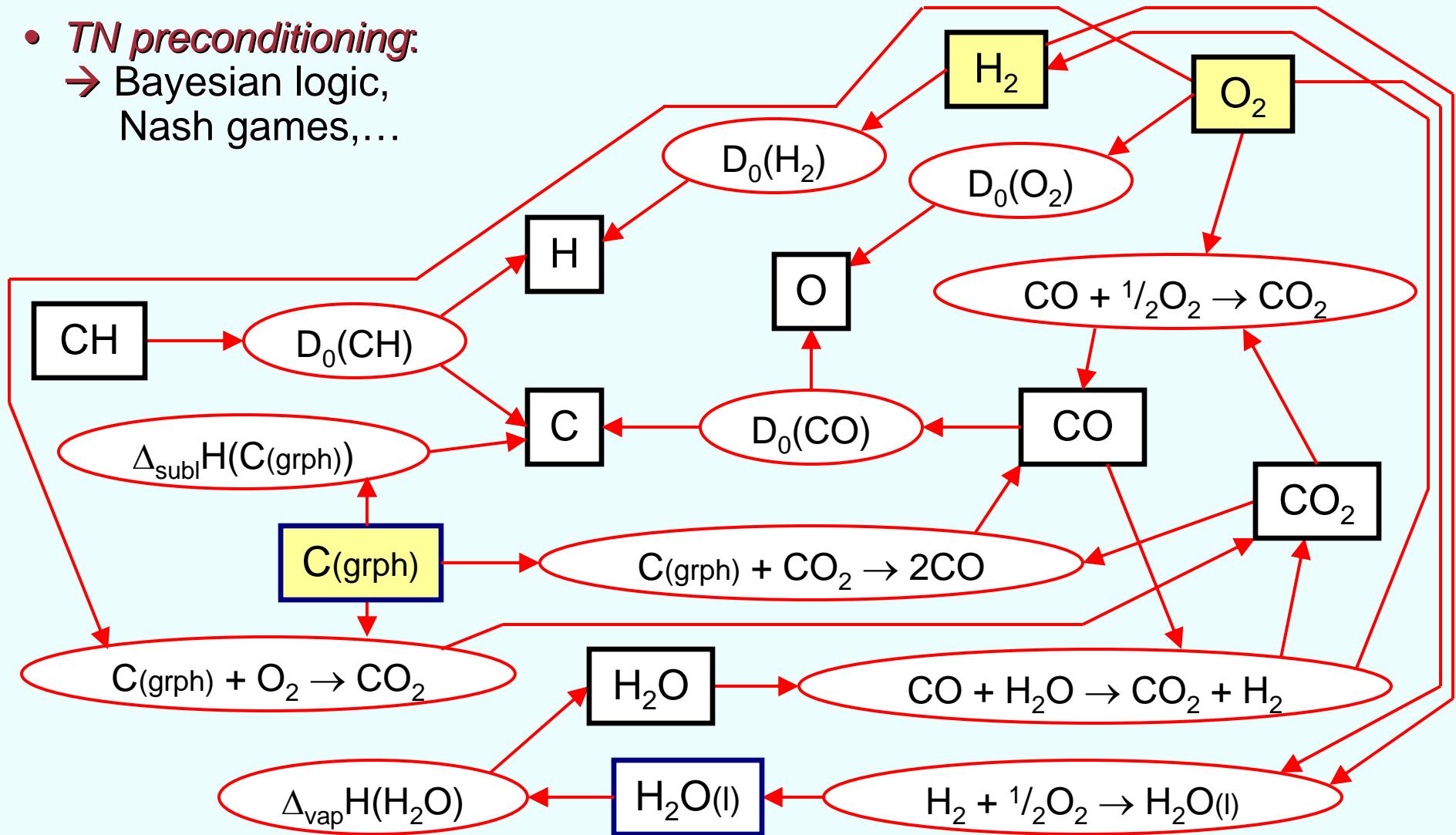


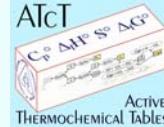
SOLVING THE THERMOCHEMICAL NETWORK



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- **TN preconditioning:**
→ Bayesian logic,
Nash games,...





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SOME ADVANTAGES OF ACTIVE THERMOCHEMICAL TABLES

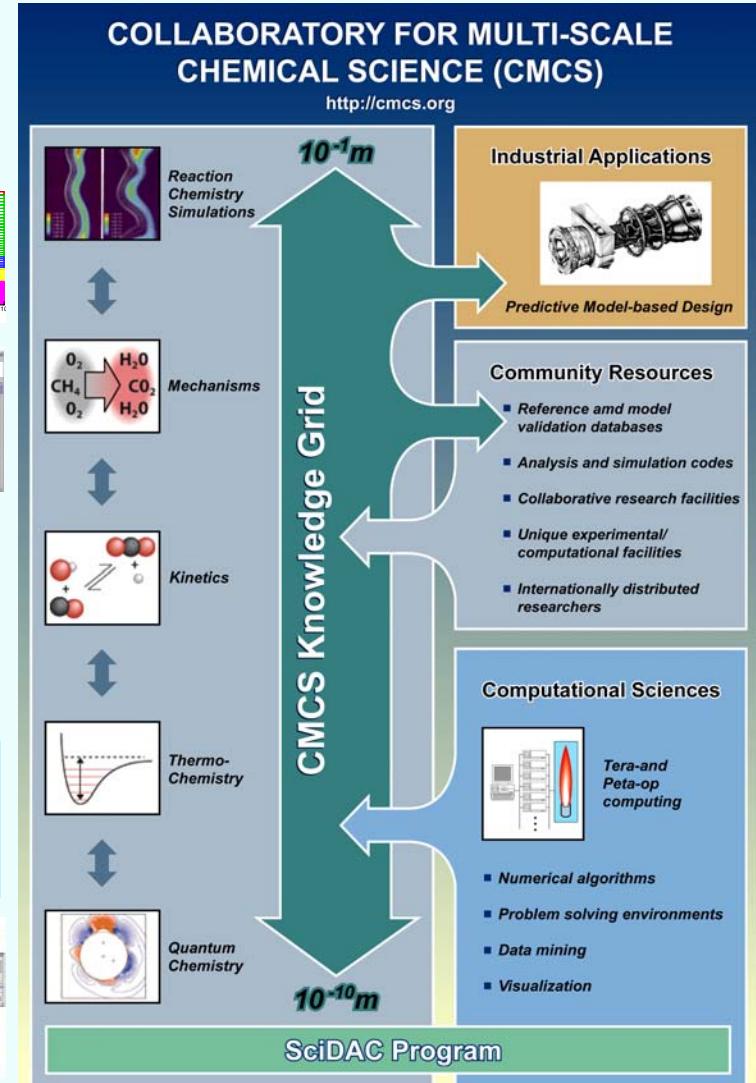
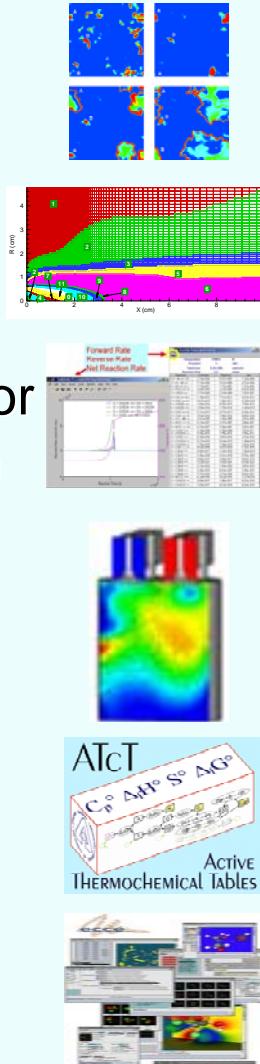
- The solutions ($\Delta_f H^\circ$'s) are **superior** to conventional tables:
 - values are **globally consistent** with all input data
 - **uncertainties properly reflect all relationships** presented as input
- Allows painless **propagation of new data** with all its consequences
 - Opens a new venue of **rapid availability of latest information** (including tentative data, if so desired)
- Allows "**what if**" **tests** of:
 - **new data** for consistency (or lack thereof) with existing knowledge
 - **educational explorations**, including hypothetical data
- By finding the "**weakest links**" in the Network it can **suggest new experiments/calculations** that will have the highest impact on current knowledge (**by itself a new paradigm**)
- Supporting documents relating to input data (raw data, notes, pdf's of papers, other pedigree information) are easily incorporated for examination



Collaboratory for Multi-scale Chemical Science (CMCS)



- CMCS is one of the **SciDAC National Collaboratories**
- Brings together scientists from various fields to develop an **open knowledge grid** and the associated **community portal** for multi-scale chemistry research
- Uses **advanced collaboration, data management and annotation technologies**
- The goal is to conquer current barriers to **rapid sharing of validated information**

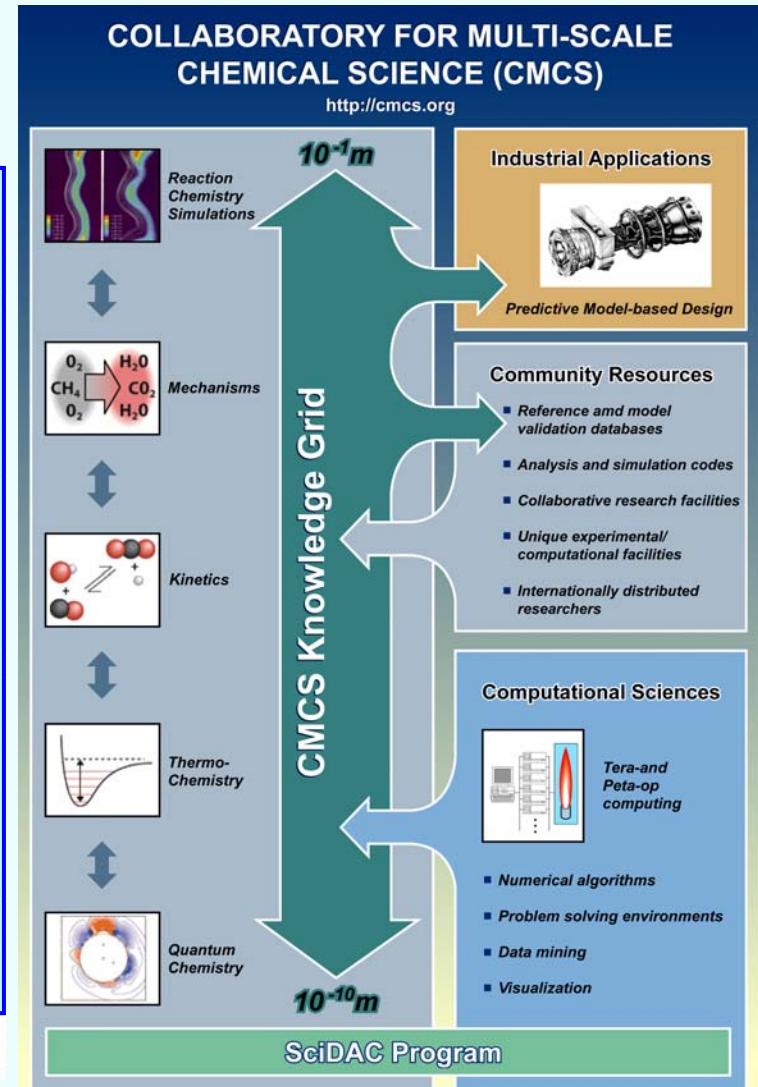
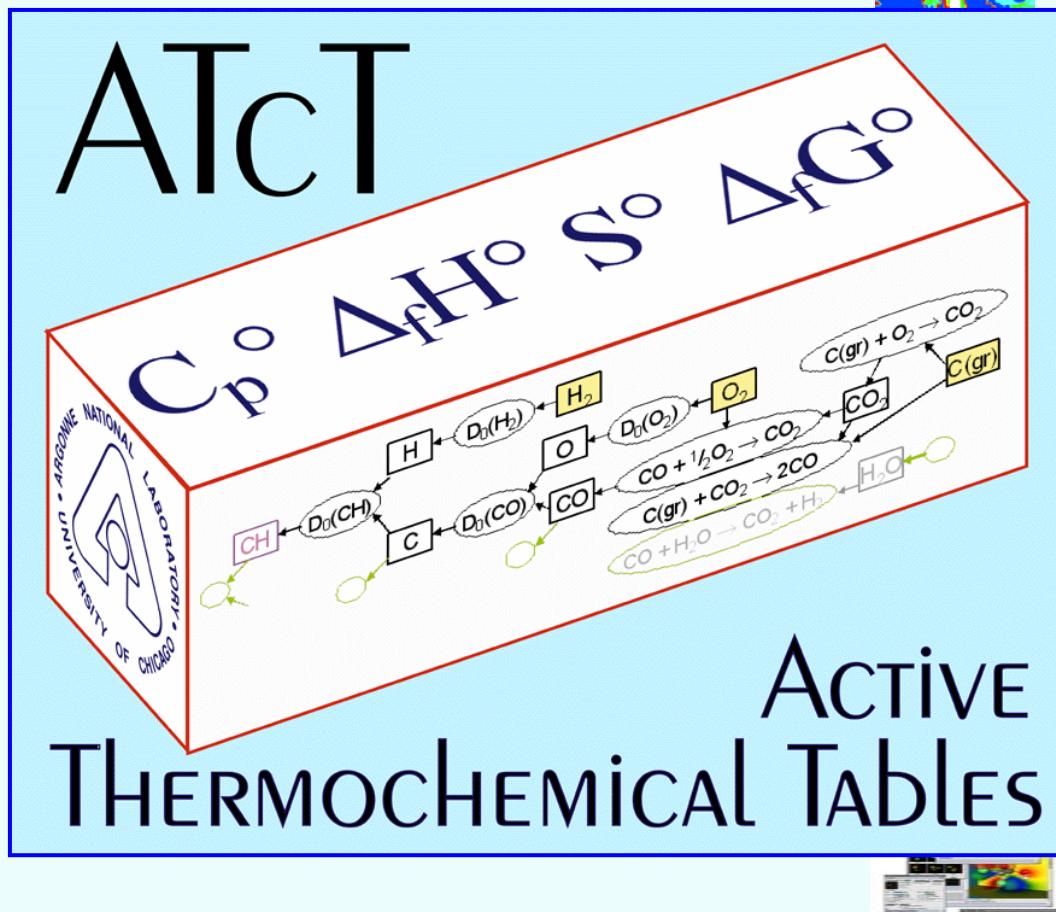
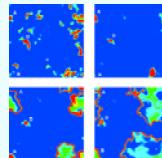




Collaboratory for Multi-scale Chemical Science (CMCS)

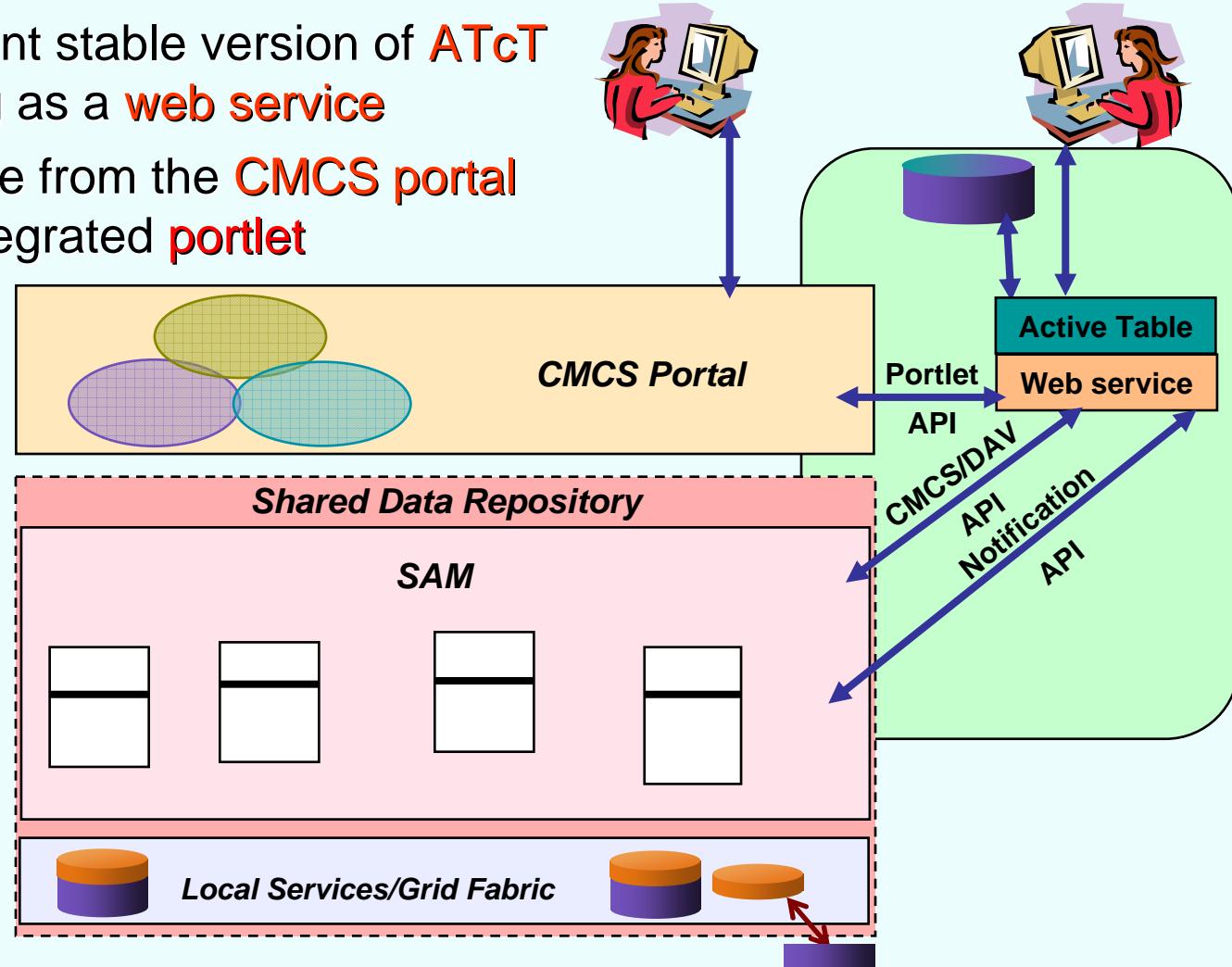


- CMCS is one of the SciDAC National Collaboratories



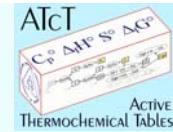
ACTIVE THERMOCHEMICAL TABLES

- The current stable version of ATcT is running as a **web service**
- Accessible from the CMCS portal via an integrated **portlet**





ACTIVE THERMOCHEMICAL TABLES



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The Collaboratory for the Multiscale Chemical Sciences (CMCS) will bring together leaders in scientific research and technological development across multiple DOE laboratories, other government laboratories and academic institutions to develop an informatics-based approach to synthesizing multi-scale information to create knowledge in the chemical sciences. CMCS has integrated advanced collaboration and metadata-based data management technologies to develop this MCS (Multi-scale Chemical Sciences) portal providing community communications mechanisms and data search and annotation capabilities.

Multi-Scale Chemical Science

- Quantum Chemistry
- Thermo-Chemistry
- Kinetics
- Mechanisms
- Reaction Chemistry Simulations

10⁻¹⁰m 10⁻¹m

CMCS (dev-local): Website - Microsoft Internet Explorer

Collaboratory for Multi-Scale Chemical Science

Active Tables

ATcT

This portlet lets you query thermochemical data for the species you enter.

Chemical species: CH4

CMCS Explorer Portlet

Address: http://cmcs.ca.sandia.gov:9080/files/projects/prime

Users Present: Branko Ristic

Resource

- Contributions
- KineticsWG
- NaturalGasWG
- NitrogenWG
- ThermochemistryWG
- TransportWG

CMCS News

- 11/16-11/22 SC2002 Baltimore, MD
- 02/28/03 CMCS Development Release 2
- 03/03/03 CMCS Advisory Board Meeting
- 06/18/03 CMCS Workshop

Local intranet



- The current version is running.
- Accessible via an interface.

CMCS (dev-local): Worksite - Microsoft Internet Explorer

File Edit View Favorites Tools Help

Back Search Favorites Media Go Links

Address http://cmcs.ca.sandia.gov:10081/cmcs/portal/group/prime/page/default.psm!/js_pane/P-f48d1e2585-10004

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April 28, 2003 08:09 am

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ATct

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Active Tables

ATct

This portlet lets you query thermochemical data for the species you enter.

WebDAV Options Reaction network Get Cleanup About AJMenu

Chemical species GO!

For example: CH4

2229-07-4
CH3 <g>
Methyl radical

Molecular weight: 15.03452 +- 0.00083

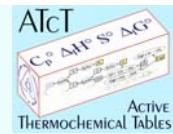
Preferred enthalpy of formation:
149.960 +- 0.370 kJ/mol at 0.000 K [MainLibrary:solve] (ver. 0.004)

Alternate value(s) for enthalpy of formation:
146.300 +- 0.500 kJ/mol at 298.150 K [GurvichLibrary:5] (ver. 0.001)
149.687 +- 0.500 kJ/mol at 0.000 K [GurvichLibrary:5] (ver. 0.001)
145.687 +- 0.800 kJ/mol at 298.150 K [JANAFLibrary:6] (ver. 0.001)
149.031 +- 0.800 kJ/mol at 0.000 K [JANAFLibrary:6] (ver. 0.001)

Reference temperature is 298.15 K
Reference pressure is 100000 Pa

T K	Cp J/mol/K	S J/mol/K	H(T)-H(ref) kJ/mol	DHF(T) kJ/mol	DGF(T) kJ/mol
0.00	0.000	5.763	-10.366	149.960	149.960
200.00	35.400	179.323	-3.620	147.779	148.352
250.00	36.892	187.380	-1.813	147.195	148.561
298.15	38.417	194.008	0.000	146.571	148.880
300.00	38.477	194.245	0.071	146.546	148.895
350.00	40.120	200.300	2.036	145.865	149.340
400.00	41.780	205.765	4.083	145.175	149.883
450.00	43.420	210.781	6.214	144.486	150.513
500.00	45.023	215.439	8.425	143.805	151.220
600.00	48.100	223.922	13.082	142.493	152.827
700.00	51.029	231.559	18.040	141.272	154.647
800.00	53.820	238.557	23.284	140.165	156.635
900.00	56.456	245.050	28.799	139.184	158.754
1000.00	58.910	251.126	34.569	138.326	160.976
1100.00	61.164	256.849	40.574	137.580	163.278
1200.00	63.210	262.260	46.794	136.934	165.643
1300.00	65.052	267.393	53.209	136.370	168.059
1400.00	66.702	272.276	59.798	135.874	170.515
1500.00	68.174	276.929	66.544	135.432	173.005
1600.00	69.485	281.371	73.428	135.034	175.523
1700.00	70.653	285.620	80.436	134.670	178.065
1800.00	71.693	289.688	87.554	134.331	180.628
1900.00	72.621	293.589	94.771	134.009	183.209
2000.00	73.449	297.336	102.075	133.700	185.806
2100.00	74.192	300.938	109.458	133.397	188.419
2200.00	74.857	304.405	116.911	133.096	191.046
2300.00	75.456	307.746	124.427	132.794	193.687
2400.00	75.996	310.969	132.000	132.487	196.341
2500.00	76.483	314.081	139.624	132.173	199.008

Local intranet



ATct





- The current version is running
- Accessible via an interface

CMCS (dev-local): Worksite - Microsoft Internet Explorer

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Address http://cmcs.ca.sandia.gov:10081/cmcs/portal/group/prime/page/default.psm!/js_pane/P-f48d1e2585-10004

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Active Tables

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This portlet lets you query thermochemical data for the species you enter.

WebDAV Options Reaction network Get Cleanup About AJMenu

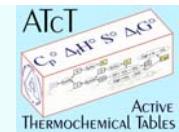
Chemical species Go!

For example: CH4

{CH2 <g>, singlet>, 2465-56-7*2, Methylene} + {H2O <g>, 7732-18-5*0, Water} -> {CH3 <g>, 2229-07-4, Methyl radical} + {OH <g>, 3352-57-6, Hydroxyl radical}

T K	S J/mol/K	H(T)-H(ref) kJ/mol	DHf(T) kJ/mol	DGf(T) kJ/mol	log Keq(T)
0.00	5.763	0.666	-1.573	-1.573	infinity
200.00	-0.317	-0.009	-2.248	-2.185	0.5705
250.00	-0.393	-0.026	-2.264	-2.166	0.4525
298.15	-0.301	0.000	-2.239	-2.149	0.3764
300.00	-0.296	0.002	-2.237	-2.148	0.3740
350.00	-0.091	0.068	-2.170	-2.138	0.3191
400.00	0.172	0.167	-2.071	-2.140	0.2795
450.00	0.465	0.292	-1.947	-2.156	0.2502
500.00	0.768	0.436	-1.803	-2.187	0.2284
600.00	1.364	0.764	-1.475	-2.293	0.1997
700.00	1.920	1.125	-1.114	-2.458	0.1834
800.00	2.428	1.505	-0.733	-2.676	0.1747
900.00	2.892	1.899	-0.340	-2.942	0.1708
1000.00	3.316	2.301	0.063	-3.253	0.1699
1100.00	3.702	2.706	0.468	-3.604	0.1711
1200.00	4.053	3.110	0.871	-3.992	0.1738
1300.00	4.370	3.507	1.268	-4.414	0.1773
1400.00	4.656	3.892	1.654	-4.865	0.1815
1500.00	4.912	4.262	2.024	-5.344	0.1861
1600.00	5.138	4.613	2.374	-5.846	0.1909
1700.00	5.337	4.940	2.702	-6.370	0.1957
1800.00	5.509	5.243	3.004	-6.913	0.2006
1900.00	5.658	5.518	3.279	-7.472	0.2054
2000.00	5.785	5.765	3.526	-8.044	0.2101
2100.00	5.891	5.983	3.744	-8.628	0.2146
2200.00	5.980	6.172	3.934	-9.222	0.2189
2300.00	6.051	6.334	4.095	-9.823	0.2231
2400.00	6.109	6.468	4.229	-10.431	0.2270
2500.00	6.153	6.576	4.337	-11.045	0.2308
2600.00	6.186	6.660	4.421	-11.662	0.2343
2700.00	6.209	6.721	4.483	-12.281	0.2376
2800.00	6.224	6.762	4.524	-12.903	0.2407
2900.00	6.231	6.784	4.545	-13.526	0.2436
3000.00	6.233	6.789	4.550	-14.149	0.2464
3100.00	6.230	6.779	4.540	-14.772	0.2489
3200.00	6.222	6.755	4.517	-15.395	0.2513
3300.00	6.212	6.720	4.482	-16.017	0.2535
3400.00	6.198	6.676	4.437	-16.637	0.2556

Local intranet



ATct





- The current version is running
- Accessible via an interface

CMCS (dev-local): Worksite - Microsoft Internet Explorer

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Active Tables ATCT

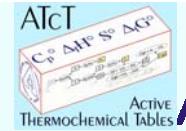
This portlet lets you query thermochemical data for the species you enter.

Reaction network

Chemical species GO!

The diagram illustrates a reaction network with various chemical species represented as nodes and their interactions as edges. Nodes include OH+, OH, H2O, H2O2, H2O(l), H2O2(l), H, O, O2, and H2. Edges are color-coded and numbered:

- Blue edges (top row):
 - OH → OH+ (20, 21, 22, 22a)
 - H2O → OH+ (16, 17, 18, 19)
 - H2O2 → OH+ (10, 11, 12)
- Green edges:
 - OH → H2O (15)
 - OH → H (3, 4)
 - OH → O (14)
 - H2O → H (5, 6)
 - H2O → O (1)
 - H2O2 → O (10, 11, 12)
 - H2O2(l) → H2O (13)
 - H2O2(l) → O2 (13)
 - H2O(l) → H2O (5, 6)
 - H2O(l) → O2 (23)
 - H2O(l) → H (2)
 - H2O(l) → H (7, 8, 9)
 - H2O(l) → O (1)
 - H2O(l) → O (23)
 - H2O(l) → H2 (2)
 - H2O(l) → O2 (1)
 - H2O(l) → O2 (23)
 - H2O(l) → H2 (7, 8, 9)
- Red edges:
 - OH → H (23)
 - H → H2 (2)
 - H → O2 (1)
 - H → O2 (23)
 - H → H2 (7, 8, 9)
 - O → O2 (1)
 - O → O2 (23)
- Orange edges:
 - H2O2(l) → H2 (13)
 - H2O2(l) → O2 (13)



ATCT



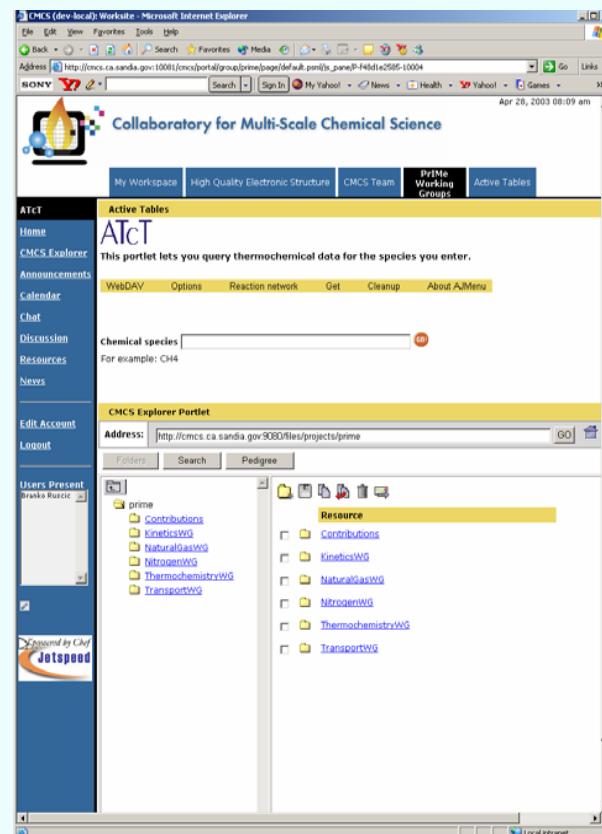


ACTIVE THERMOCHEMICAL TABLES



ATcT

- The current stable version of ATcT is running as a **web service**
- Accessible from the **CMCS portal** via an integrated **portlet**





ACTIVE THERMOCHEMICAL TABLES



- The current stable version of ATcT is running as a **web service**
- Accessible from the CMCS portal via an integrated **portlet**
- The ATcT back-end system consists of a **kernel**

CMCS (dev-local) Worksite - Microsoft Internet Explorer
Address: <http://cmcs.ca.sandia.gov:10081/cmcs/portal/group/oxin/page/default.portal?pn=oxin&f=felicitis/10004>

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Address: <http://cmcs.ca.sandia.gov:9080/files>
Folders Search Pedigree

Chemical species: CH4
For example: CH4

CMCS Explorer Portlet
Standard reference states of elements:
H def: TestNotes (0.0172), date: M0507ElementsLexicon in TestNotes (0.0172)
H def: TestNotes (0.0172), date: M0507ElementsLexicon in TestNotes (0.0172)
O def: TestNotes (0.0172), date: M0507ElementsLexicon in TestNotes (0.0172)

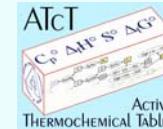
Partition function/spectral data: from data: M0507Lexicon in TestNotes (0.0172)

Reference temperature is 298.15 K
Reference pressure is 100000 Pa

T	Cp cal/mol/K	S cal/mol/K	H(C)-H(Cat) J cal/mol	DH(C) J cal/mol	DH(C) J cal/mol
0.00	0.000	0.000	-3.093	-27.121	-37.474
100.00	out of range	out of range	out of range	out of range	out of range
250.00	12.091	50.862	-6.609	-29.282	-32.984
298.15	13.222	63.086	0.000	-37.677	-31.735
350.00	13.353	65.316	0.523	-37.772	-31.835
350.00	14.514	65.398	0.720	-46.092	-30.320
450.00	17.111	69.276	2.303	-46.827	-26.429
500.00	19.295	71.141	3.189	-41.158	-25.293
500.00	20.479	72.006	5.153	-42.231	-24.441
700.00	22.475	77.398	7.280	-42.231	-19.425
800.00	24.156	81.193	9.622	-42.626	-16.367
800.00	25.837	83.943	11.963	-43.177	-15.365
1000.00	26.886	86.809	14.739	-43.174	-9.733
1100.00	27.837	87.675	17.514	-43.174	-8.733
1100.00	28.975	91.391	20.371	-43.475	-3.013
1300.00	29.298	94.251	23.267	-43.558	0.362
1300.00	30.371	95.333	24.300	-43.475	-1.426
1500.00	31.091	98.487	29.355	-43.633	7.126
1500.00	31.671	100.641	32.482	-43.633	19.343
1600.00	32.094	100.543	32.482	-43.633	19.343
1600.00	32.519	104.410	38.914	-43.610	17.278
1600.00	32.843	106.172	40.241	-43.583	17.278
2000.00	33.297	107.473	45.489	-43.503	24.940
2100.00	33.493	109.180	48.824	-43.521	23.419
2100.00	33.717	111.528	52.157	-43.540	33.795
2300.00	33.975	112.570	55.573	-43.469	34.172
2400.00	34.178	114.020	58.981	-43.434	37.547



ACTIVE THERMOCHEMICAL TABLES



ATcT

- The current stable version of ATcT is running as a **web service**
- Accessible from the CMCS portal via an integrated **portlet**
- The ATcT back-end system consists of a **kernel** and the **underlying collection of thermochemically relevant data**

The screenshot displays the ATcT software environment. On the left, a Windows-style file browser window titled 'D:\ATcT' shows various note and library folders. On the right, a Microsoft Internet Explorer window titled 'CMCS (dev-local) Worksite - Microsoft Internet Explorer' shows the ATcT portlet within the CMCS portal. The portlet interface includes a search bar, a list of recent queries, and a detailed search results table. The table lists chemical species and their properties, such as enthalpies of formation (Hf), standard enthalpies of combustion (DHf), and standard entropies (Sf). A portion of the table is as follows:

	Hf (kJ/mol)	DHf (kJ/mol)	Sf (J/mol K)
NH	-3.083	-27.121	-37.476
He	out of range	out of range	out of range
C2	-0.609	-2.242	-32.984
CH4	0.000	-37.677	-31.735
CH3CHO	0.233	-37.772	-31.855
CH3CO	0.720	-46.092	-30.320
CH3COOH	2.303	-46.827	-37.429
Li	3.189	-41.158	-25.923
LiK	5.35	-42.231	-24.944
LiH	7.280	-42.231	-19.425
LiCl	9.622	-42.626	-16.367
LiBr	11.177	-42.626	-16.367
LiI	14.739	-43.174	-9.733
LiF	14.739	-43.174	-9.733
LiAl	20.371	-43.475	-3.013
LiGa	23.267	-43.558	0.362
LiIn	23.267	-43.558	0.362
LiCd	23.700	-43.700	1.413
LiAl ₃	29.355	-43.633	7.126
LiGa ₃	32.682	-43.633	19.344
LiIn ₃	32.682	-43.633	19.344
LiCd ₃	32.682	-43.633	19.344
LiAl ₂	38.914	-43.610	17.278
LiGa ₂	38.914	-43.610	17.278
LiIn ₂	38.914	-43.610	17.278
LiCd ₂	45.489	-43.503	24.940
LiAl ₄	49.824	-43.521	25.419
LiGa ₄	49.824	-43.521	25.419
LiIn ₄	49.824	-43.521	25.419
LiCd ₄	55.570	-43.449	34.172
LiAl ₅	58.981	-43.434	37.547
LiGa ₅	58.981	-43.434	37.547
LiIn ₅	58.981	-43.434	37.547
LiCd ₅	58.981	-43.434	37.547

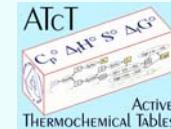


ACTIVE THERMOCHEMICAL TABLES



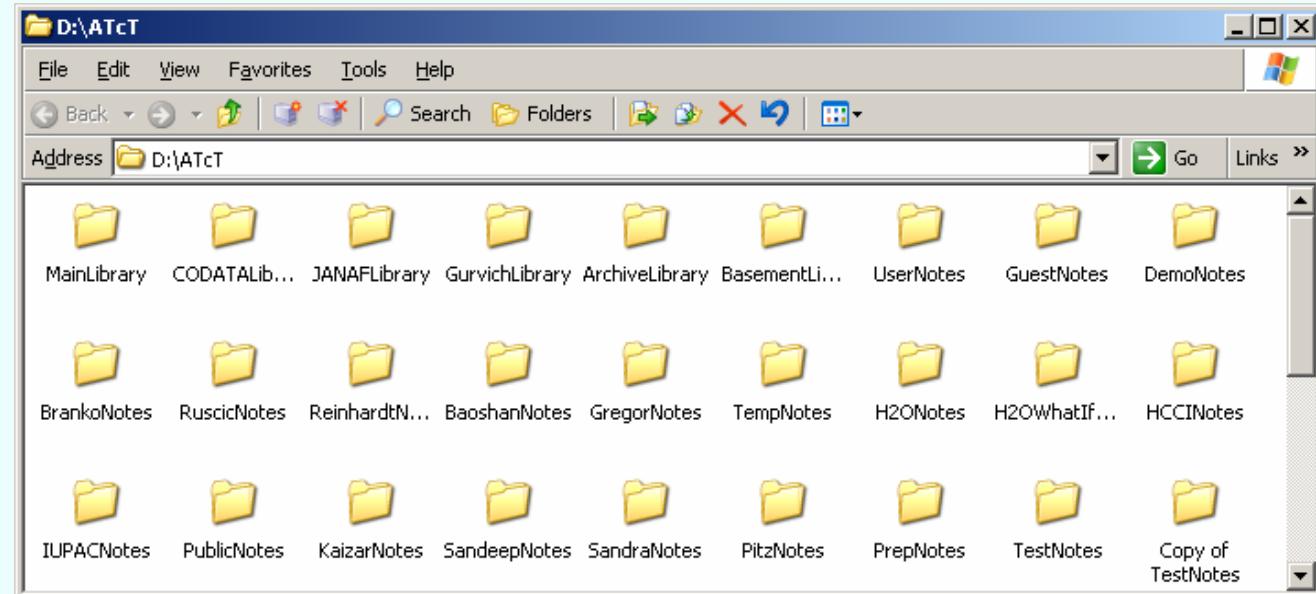
- The current stable version of ATcT is running as a **web service**
 - Accessible from the CMCS portal via an integrated **portlet**
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- D:\ATcT**
- File Edit View Favorites Tools
- Address D:\ATcT
- MainLibrary CODATALib... JANALibr
- BrankoNotes RuscicNotes Reinhardt
- IUPACNotes KaizerNotes PitzNote
- ATcT - Eclipse Visual Editor**
- My Workspace High Quality Electronic St hit # 1: 25-97-B CH3CHO
Beta-aldehyde found in: TestNotes <ver. 8.01>
- hit # 2: 25-21-B
- ATcT (dev-local) Worksite - Microsoft Internet Explorer**
- Address http://cmcs.ca.sandia.gov:10081/cmcs/portal/group/brinw/page/default.pml?jsn_pane1=598-10004
- SONY YZ+ Search Sign In My School News Health Yahoo Games
- ATcT Command Prompt - qgenqne
- hit # 1: 25-97-B CH3CHO Beta-aldehyde found in: TestNotes <ver. 8.01>
- hit # 2: 25-21-B
- ATcT - Debug - Find in File 1 > Find in File 2 > Results - SQL Debugging**
- Ready
- 2 490.00 34.178 114.020 58.781 -43.434 37.547
- The ATcT kernel is quite complex; it is internally modular (eases program maintenance) and has so far ~ **60,000 lines** of Fortran 95 code (modifiable to HPF, which runs on parallel clusters, needed for handling large networks)

ATcT DATA ORGANIZATION



ATcT

- The underlying data is organized in a number of **Libraries** and **Notes**

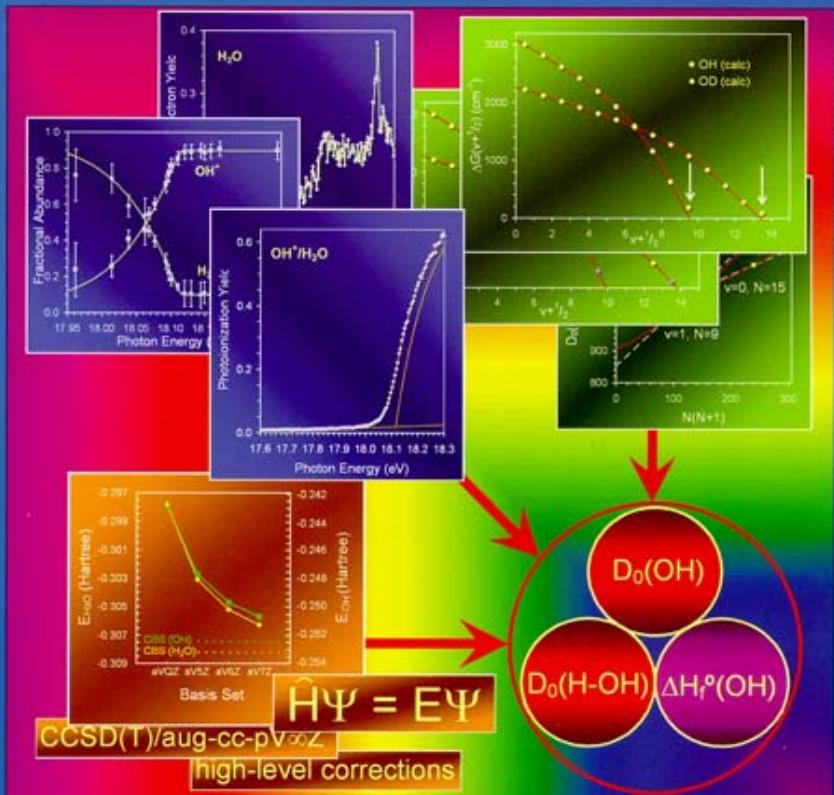


- Libraries** are large collections of data, typically generated by **committees who oversee and anoint their scientific soundness**
- Notes** are lighter versions of Libraries, typically associated with **individual users** or **collaborative workgroups**
- Main Library** contains the **Core (Argonne) Thermochemical Network**
- Auxiliary Libraries** contain data that reproduce information in historical “static” **tables** for ready reference

VOLUME 106
MARCH 21, 2002
NUMBER 11

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MOLECULES, SPECTROSCOPY, KINETICS, ENVIRONMENT, & GENERAL THEORY

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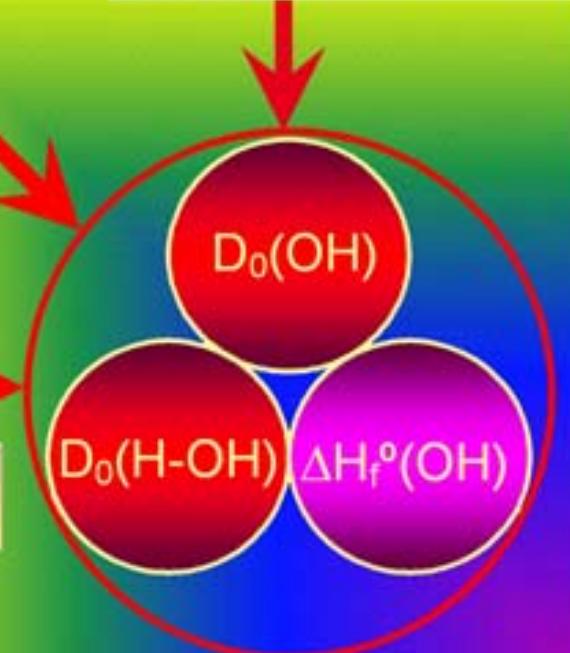
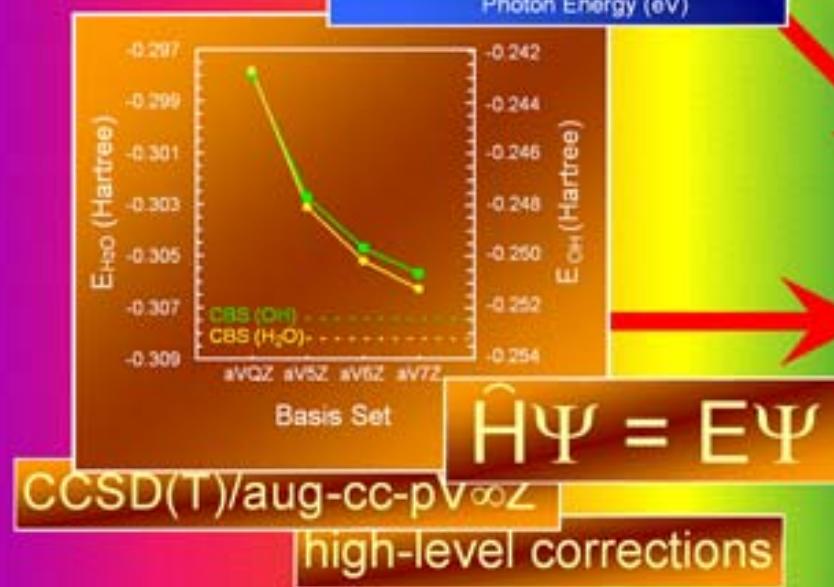
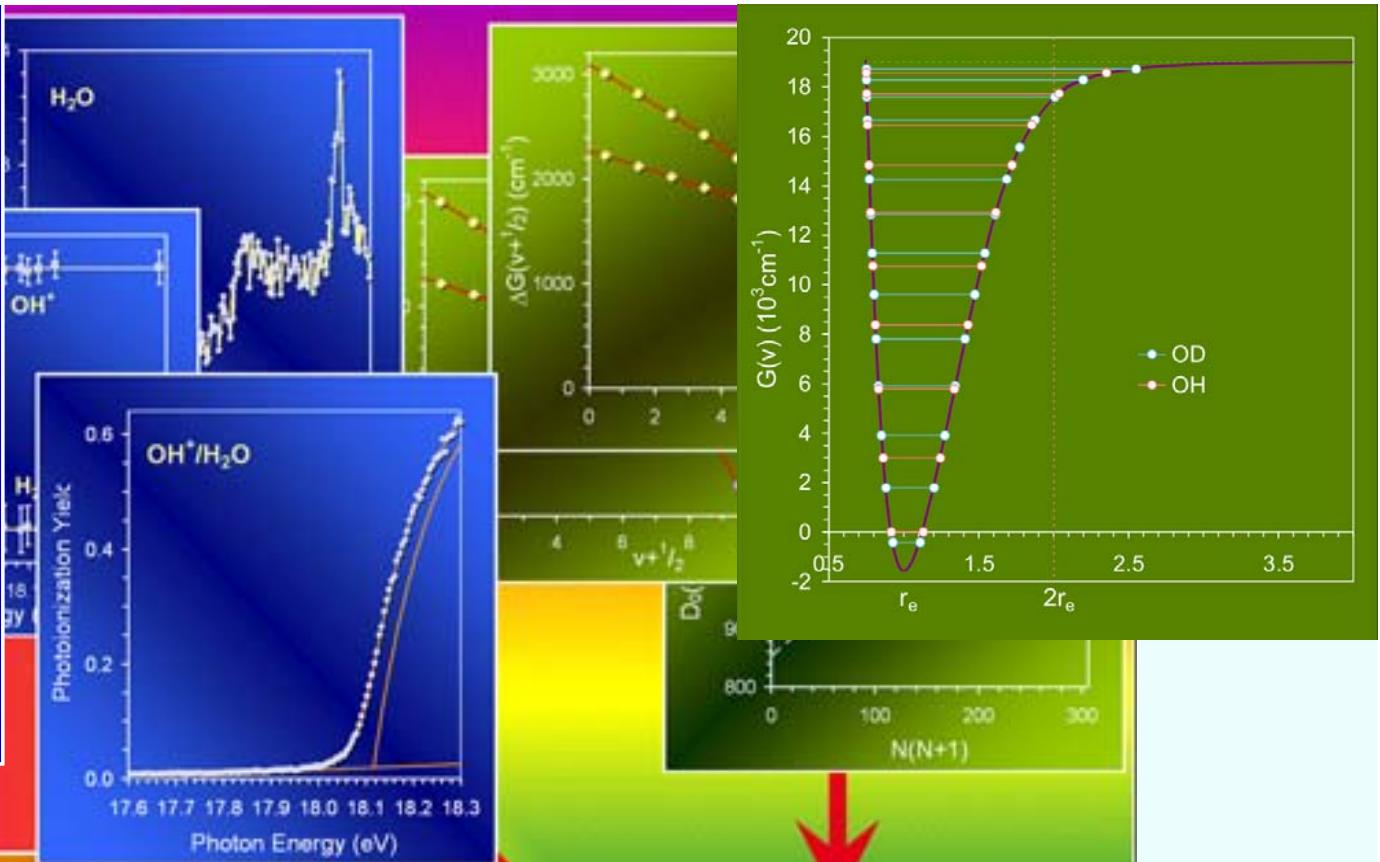
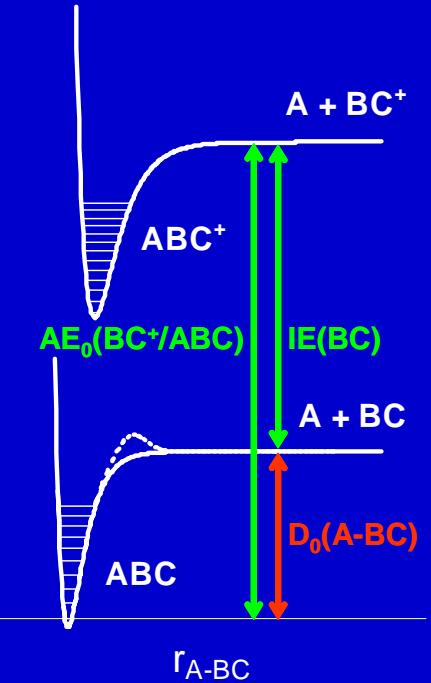
- $H_2O \rightarrow H + OH$
 $D_0(H-OH)$
- $OH \rightarrow O + H$
 $D_0(OH)$
- $H_2O \rightarrow O + 2 H$
 $D_0(H-OH) + D_0(OH) \equiv \Delta H_{at}^\circ(H_2O) = 76720.7 \pm 8.3 \text{ cm}^{-1}$
- $\Delta H_{at}^\circ(H_2O)$ depends only on $\Delta H_f^\circ(H_2O)$, $\Delta H_f^\circ(H)$, $\Delta H_f^\circ(O)$

$$\Delta H_{at}^\circ(H_2O)$$



$$D_0(H-OH) \quad \uparrow \quad D_0(OH)$$

$$\Delta H_f^\circ(H)$$



FURTHER DEVELOPMENTS...

■ $\Delta H_f^\circ(\text{OH}) = 8.86 \pm 0.16 \text{ kcal/mol}$

Herbon, Hanson, Golden, Bowman (2002)

Ruscic et al. $8.85 \pm 0.07 \text{ kcal/mol}$



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Harich, Hwang, Yang, Lin, Yang, Dixon (2000)

Ruscic et al. $41128 \pm 24 \text{ cm}^{-1}$

Gurvich et al. $41301 \pm 17 \text{ cm}^{-1}$

FURTHER DEVELOPMENTS...

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Herbon, Hanson, Golden, Bowman (2002)
Ruscic et al. $8.85 \pm 0.07 \text{ kcal/mol}$ ✓

- $D_0(\text{H-OH}) = 41151 \pm 5 \text{ cm}^{-1}$
Harich, Hwang, Yang, Lin, Yang, Dixon (2000)
Ruscic et al. $41128 \pm 24 \text{ cm}^{-1}$ 23 cm^{-1}
(0.06_6 kcal/mol) $1_{00} \leftarrow 0_{00}$ 23.8 cm^{-1}

FURTHER DEVELOPMENTS...

- $\Delta H_f^\circ(\text{OH}) = 8.86 \pm 0.16 \text{ kcal/mol}$
Herbon, Hanson, Golden, Bowman (2002)
Ruscic et al. $8.85 \pm 0.07 \text{ kcal/mol}$ ✓
- $D_0(\text{H-OH}) = 41151 \pm 5 \text{ cm}^{-1}$
Harich, Hwang, Yang, Lin, Yang, Dixon (2000) 23 cm^{-1} $(0.06_6 \text{ kcal/mol})$ 23.8 cm^{-1}
Ruscic et al. $41128 \pm 24 \text{ cm}^{-1}$ $1_{00} \leftarrow 0_{00}$
- $D_0(\text{HO-OH}) = 17051.8 \pm 3.4 \text{ cm}^{-1}$
Luo, Fleming, Rizzo (1992) – but to use it we would need to rely on $\Delta H_f^\circ(\text{H}_2\text{O}_2)$

FURTHER DEVELOPMENTS...

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Herbon, Hanson, Golden, Bowman (2002)
Ruscic et al. $8.85 \pm 0.07 \text{ kcal/mol}$ ✓
- $D_0(\text{H-OH}) = 41151 \pm 5 \text{ cm}^{-1}$
Harich, Hwang, Yang, Lin, Yang, Dixon (2000) 23 cm^{-1} $(0.06_6 \text{ kcal/mol})$ 23.8 cm^{-1}
Ruscic et al. $41128 \pm 24 \text{ cm}^{-1}$ $1_{00} \leftarrow 0_{00}$
- $D_0(\text{HO-OH}) = 17051.8 \pm 3.4 \text{ cm}^{-1}$
Luo, Fleming, Rizzo (1992) – but to use it we would need to rely on $\Delta H_f^\circ(\text{H}_2\text{O}_2)$
- Joens (2001) $D_0(\text{OH})/\text{cm}^{-1}$ $\Delta H_f^\circ(\text{OH})/\text{kcal/mol}$
Ruscic et al. (prelim. letter) $35600 \pm 30 \Rightarrow 8.82_9 \pm 0.09_1$
 $D_0(\text{H-OH}) = 41141 \pm 5 \text{ cm}^{-1} \Rightarrow 35579 \pm 11 \Rightarrow 8.89_2 (\pm 0.04_0)$
 $D_0(\text{H}_2\text{O}_2) = 17051.8 \pm 3.4 \text{ cm}^{-1} \Rightarrow 35589 \pm 12 \Rightarrow 8.86_4 (\pm 0.04_2)$
 $\Delta = 0.02_8$
 $\Rightarrow 8.87_8 \pm 0.02_9$

FURTHER DEVELOPMENTS...

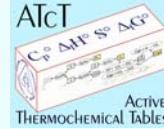
- $\Delta H_f^\circ(\text{OH}) = 8.86 \pm 0.16 \text{ kcal/mol}$
Herbon, Hanson, Golden, Bowman (2002)
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Harich, Hwang, Yang, Lin, Yang, Dixon (2000) 23 cm^{-1} $(0.06_6 \text{ kcal/mol})$ 23.8 cm^{-1}
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 $\Delta H_f^\circ(\text{H}_2\text{O}_2)$ from JANAF $\Delta = 0.02_8$
(298.15 K selection questionable,
wrong conversion to 0 K) $\Rightarrow 8.87_8 \pm 0.02_9$

FURTHER DEVELOPMENTS...

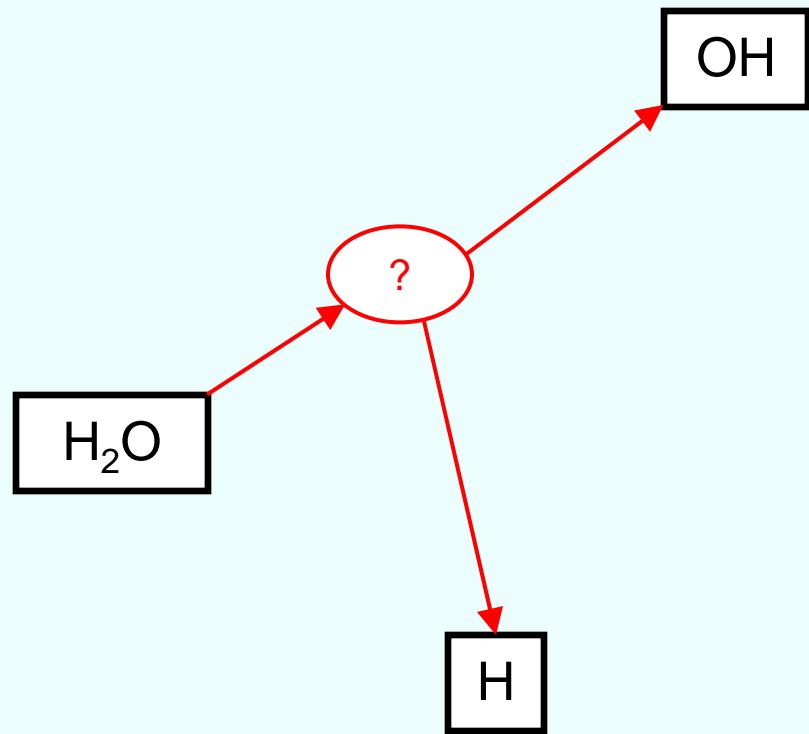
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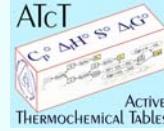
FURTHER DEVELOPMENTS...

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 $D_0(\text{H}_2\text{O}_2) = 17051.8 \pm 3.4 \text{ cm}^{-1} \Rightarrow 35589 \pm 12 \Rightarrow 8.86_4 (\pm 0.04_2) \quad 8.85_5 \pm 0.02_7$
 $\Delta H_f^\circ(\text{H}_2\text{O}_2)$ from JANAF $\Delta = 0.02_8 \quad 0.06_5$
(298.15 K selection questionable,
wrong conversion to 0 K) $\Rightarrow 8.87_8 \pm 0.02_9 \quad 8.90_0 \pm 0.38_1$



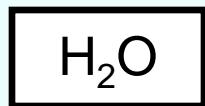
ATcT

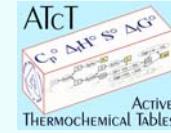




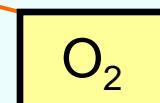
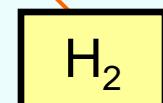
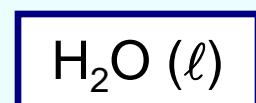
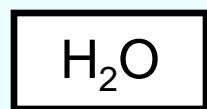
ATcT

OH

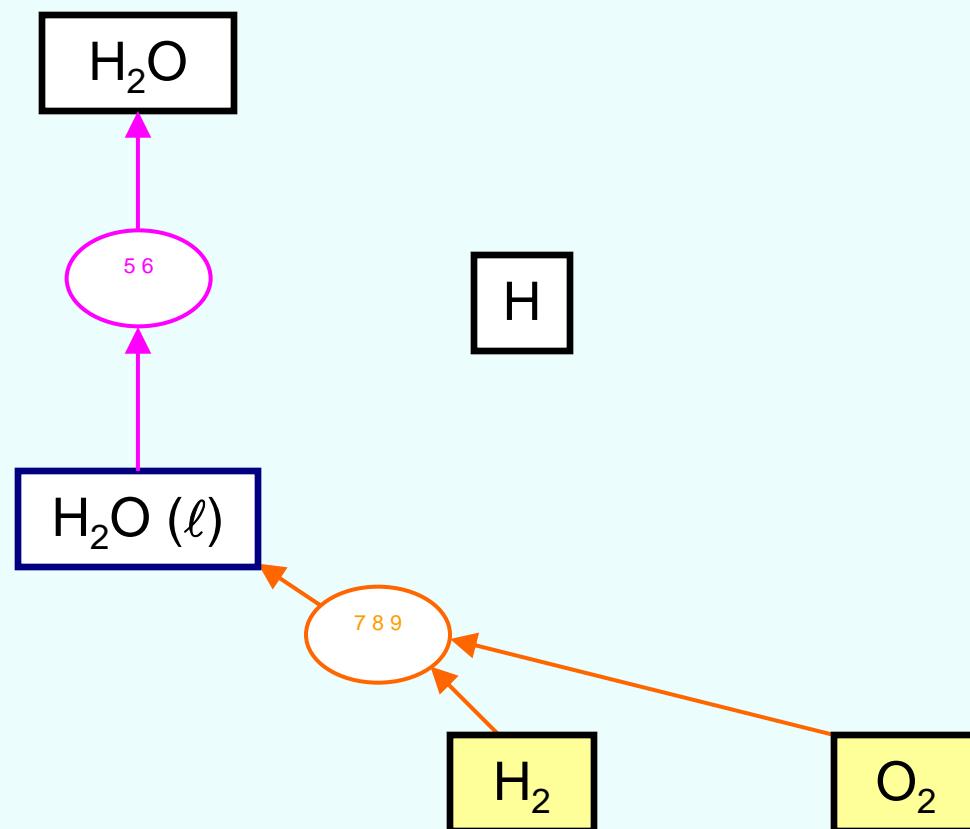


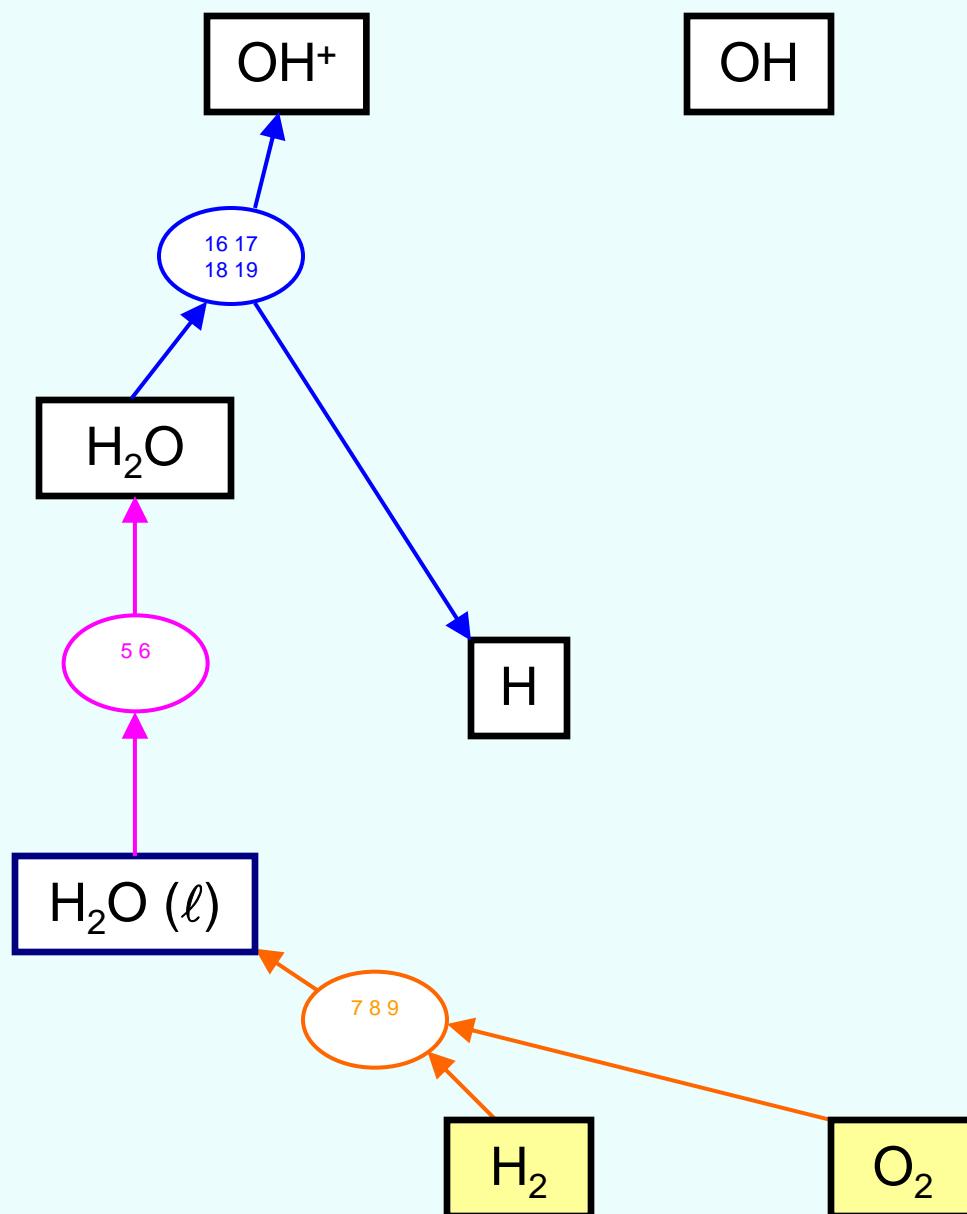


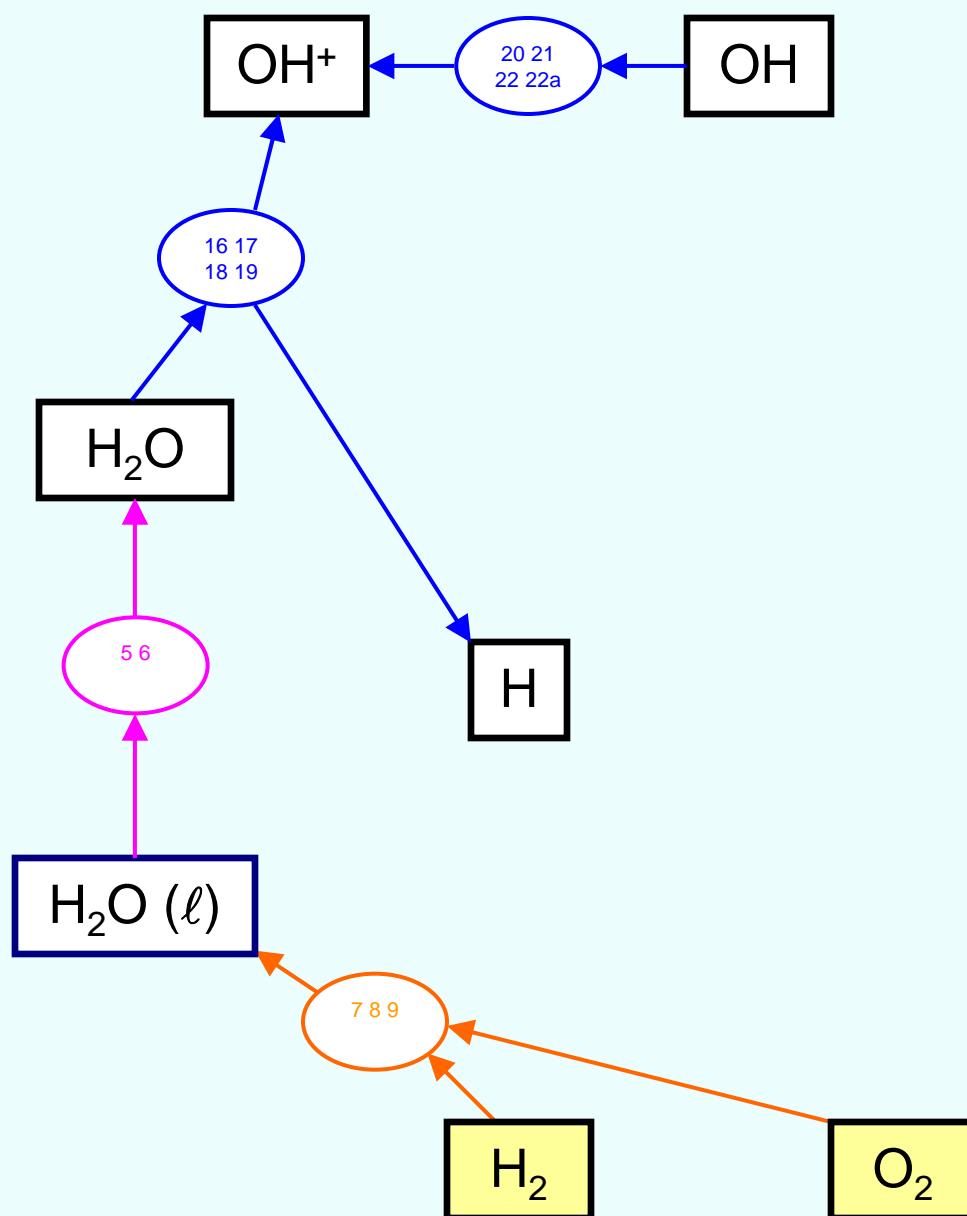
ATcT

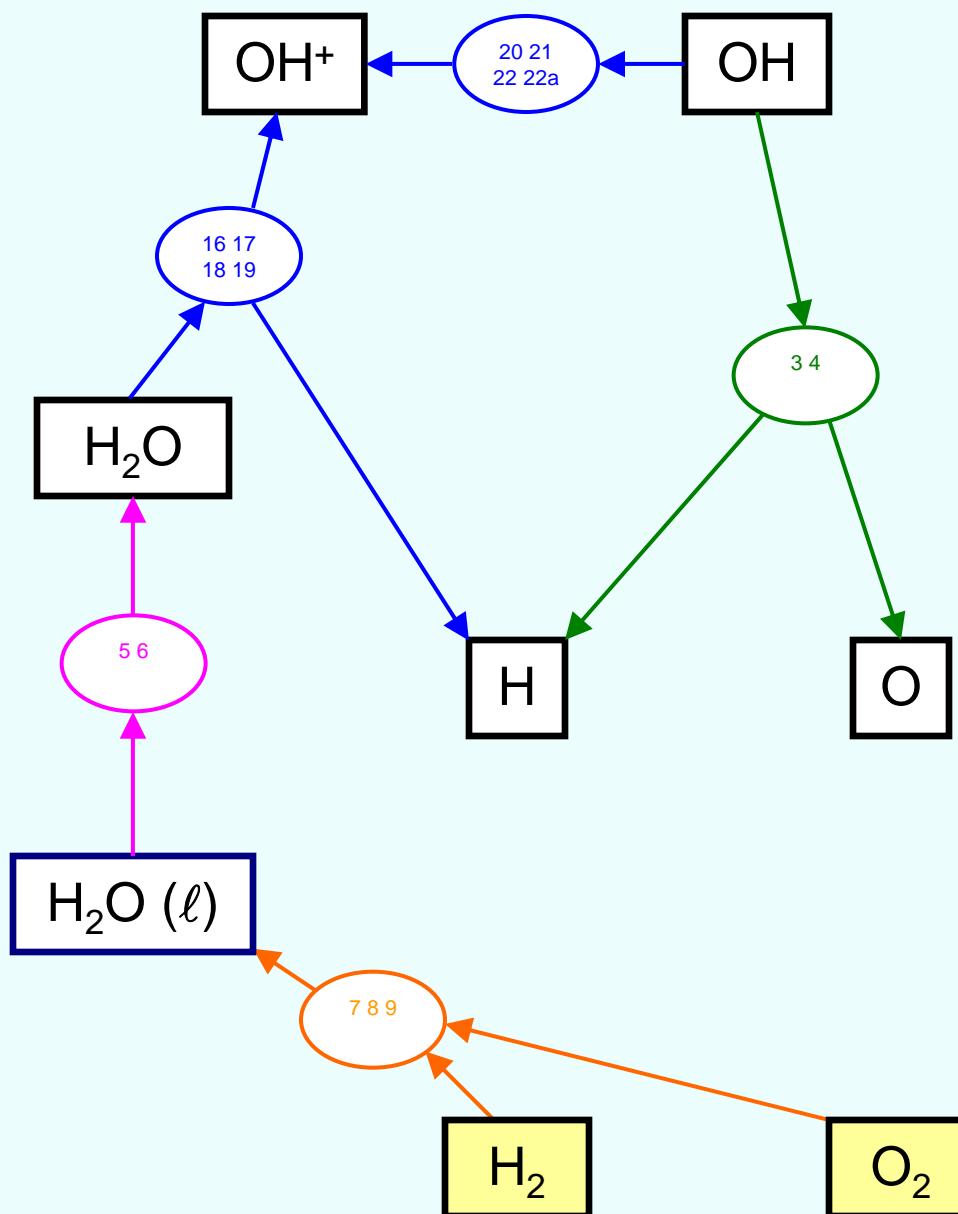


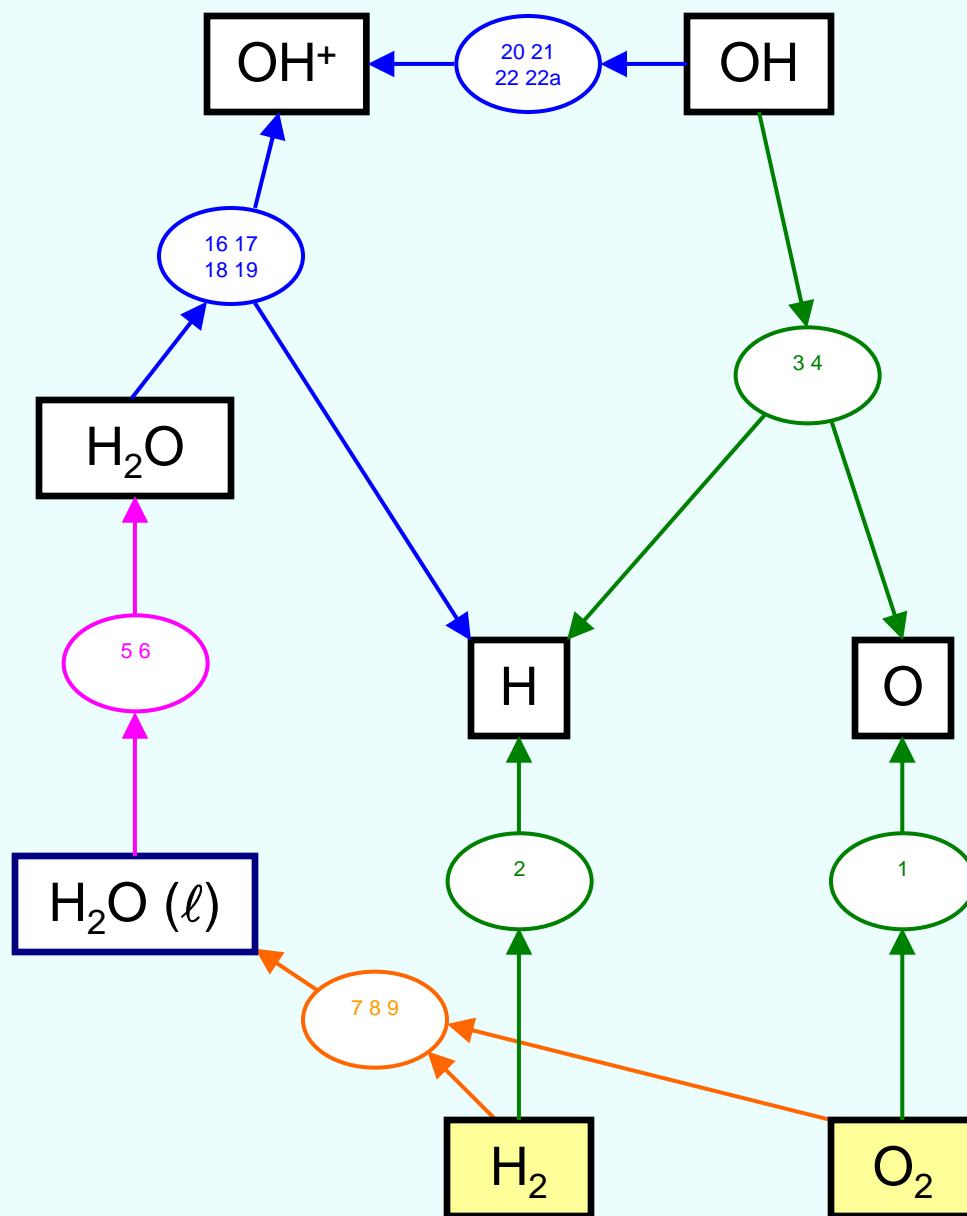
7 8 9

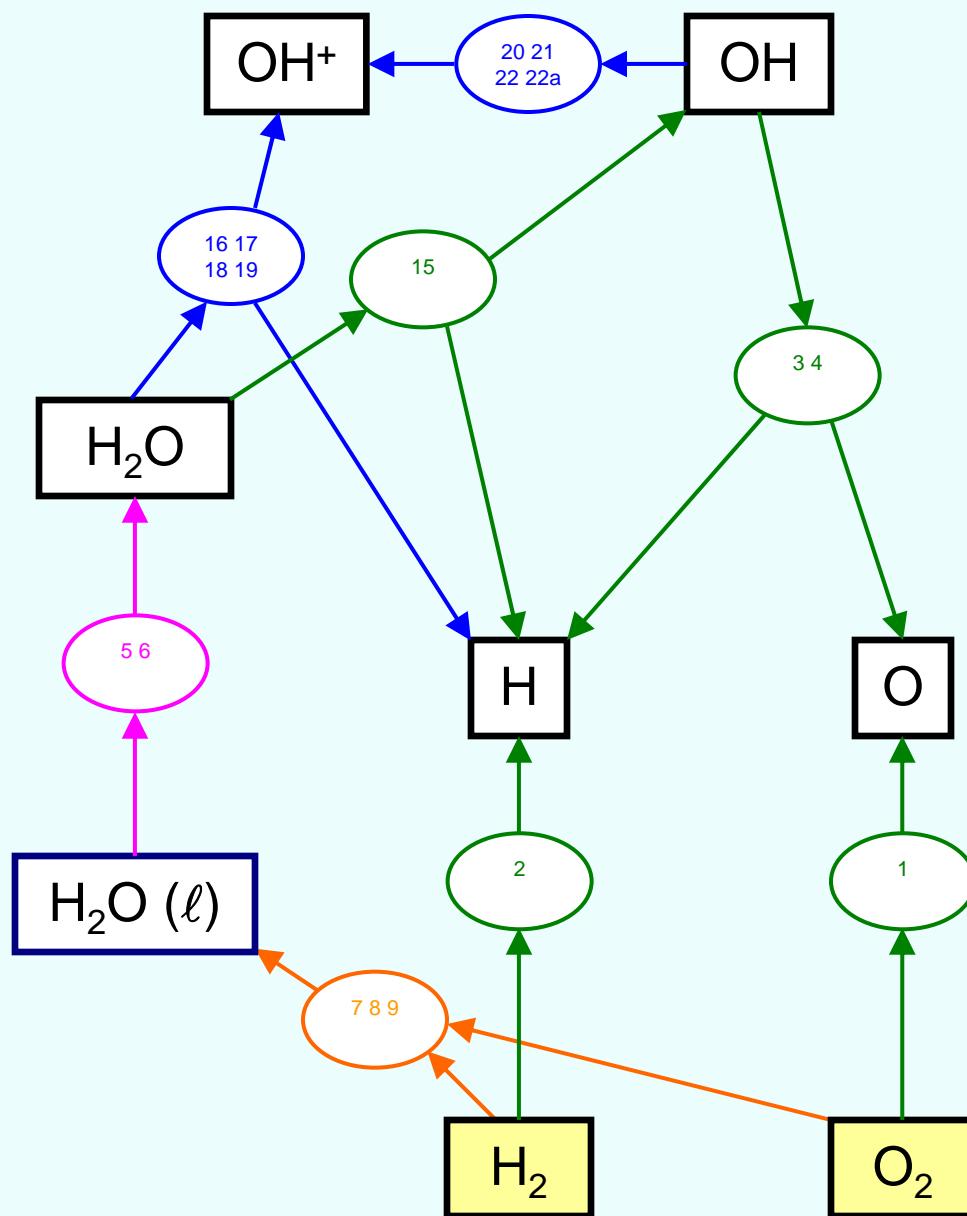


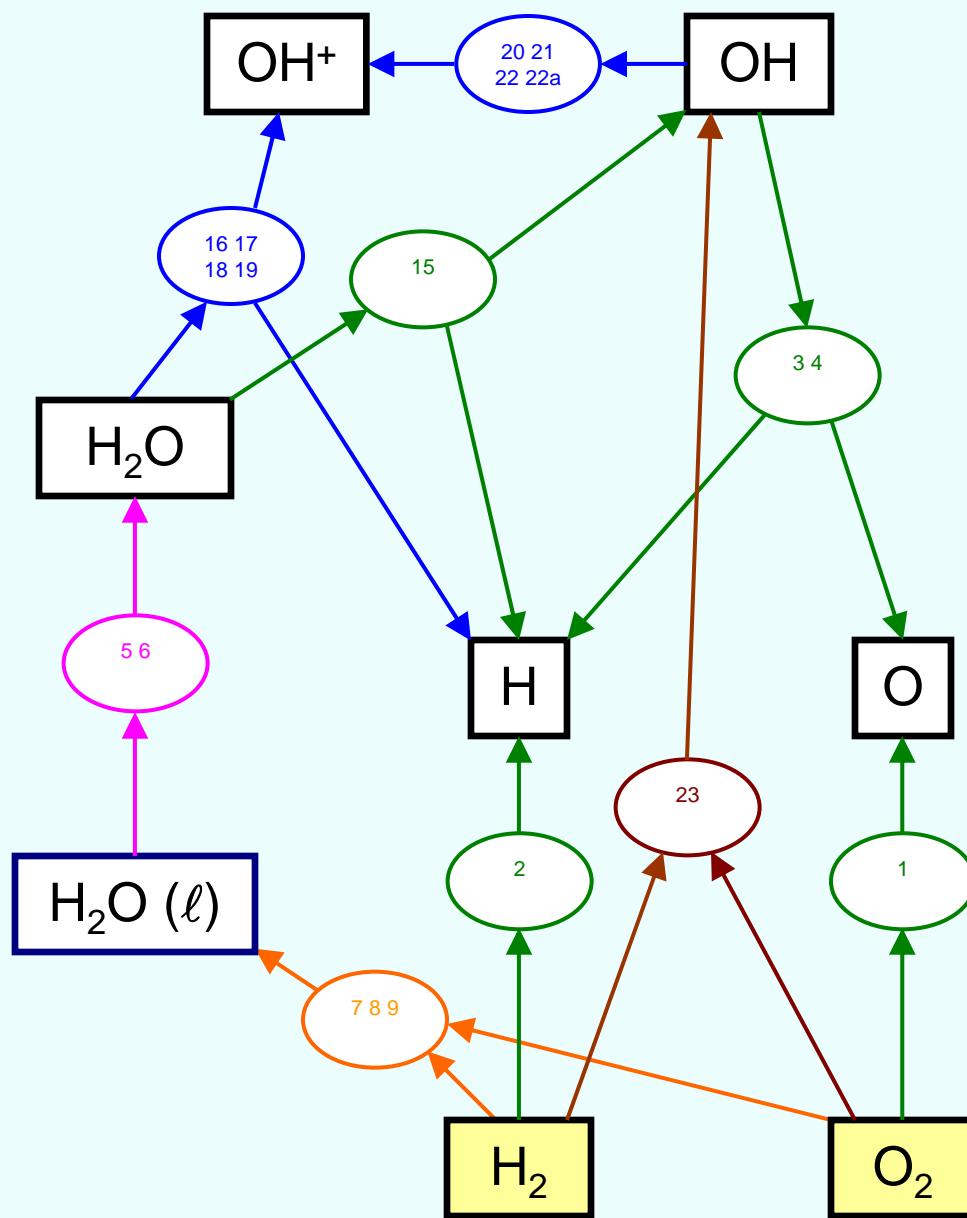


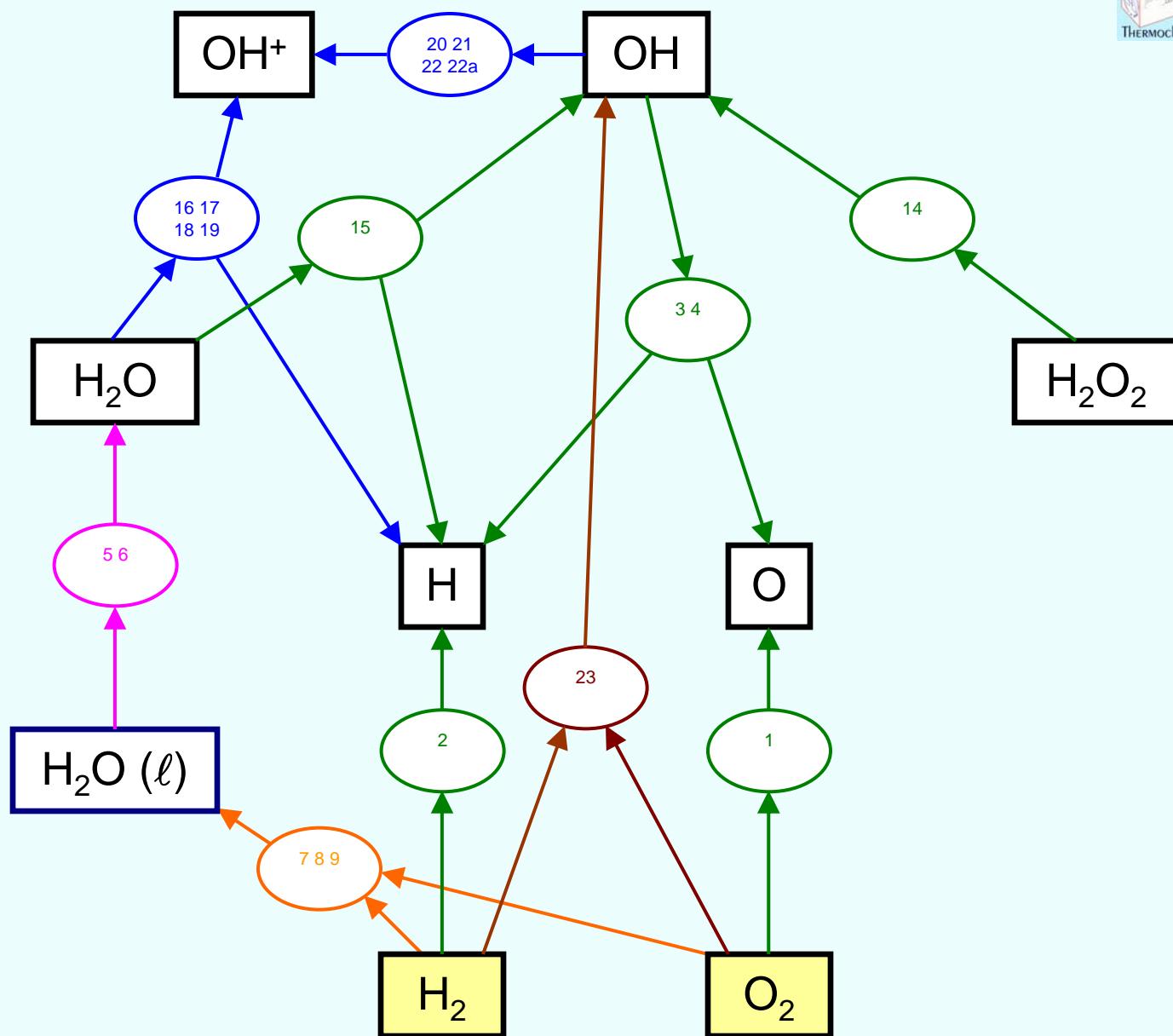


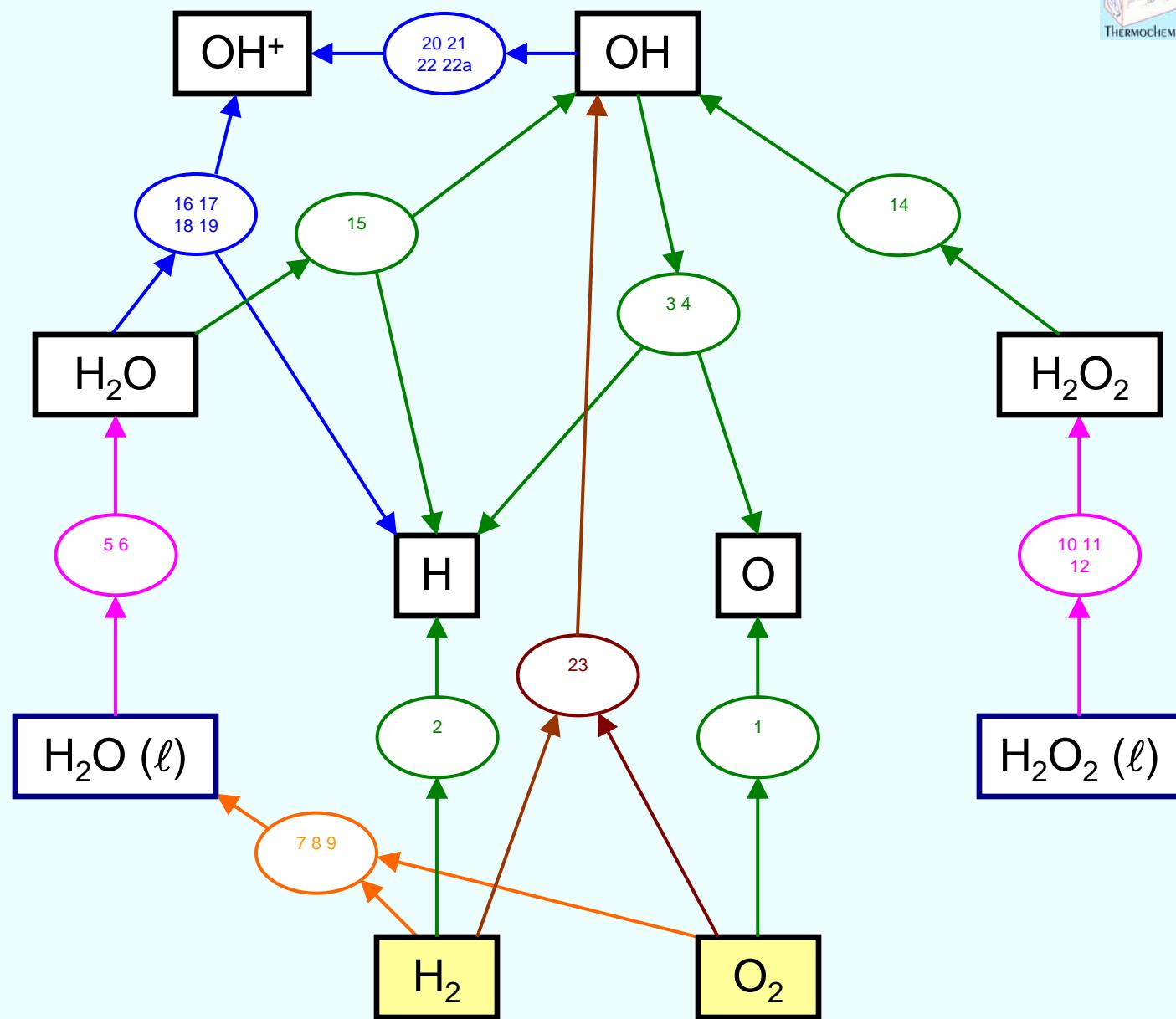


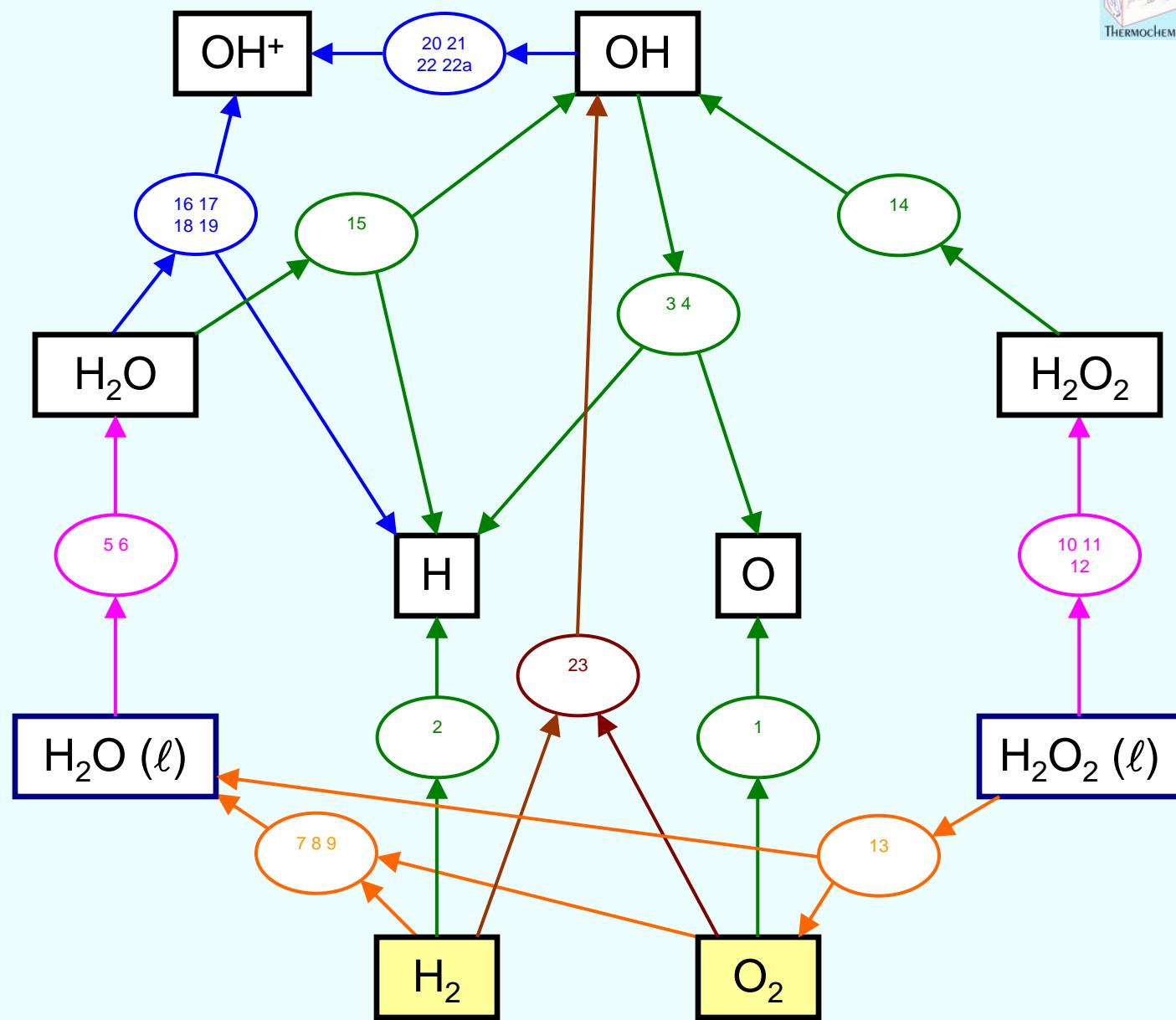












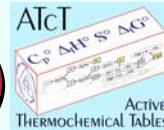
RESULTS OF ATcT O/H TN ANALYSIS



ATcT

- $\Delta H_f^\circ(\text{OH}) = \mathbf{8.85_9 \pm 0.01_7 \text{ kcal/mol}}$
(cf. Ruscic *et al.* $8.85_6 \pm 0.07_0 \text{ kcal/mol}$)
- $D_0(\text{H-OH}) = \mathbf{41129 \pm 7 \text{ cm}^{-1}}$
(cf. Ruscic *et al.* $41128 \pm 24 \text{ cm}^{-1}$)
- $D_0(\text{OH}) = \mathbf{35590 \pm 12 \text{ cm}^{-1}}$
(cf. Ruscic *et al.* $35593 \pm 25 \text{ cm}^{-1}$)
- Statistical analysis points to the following “optimistic” uncertainties:
 - $D_0(\text{OH})$, Carbone & Dalby $11.3 \times 15 \text{ cm}^{-1}$
 - $D_0(\text{H-OH})$, Harich *et al.* $4.5 \times 5 \text{ cm}^{-1}$
 - $\Delta_{\text{vap}} H^\circ_{298}(\text{H}_2\text{O}_2)$, Edgerton *et al.* 2nd Law $1.4 \times 0.74 \text{ kcal/mol}$
 - $D_0(\text{OH})$, Barrow $1.4 \times 100 \text{ cm}^{-1}$
 - $\Delta_{\text{vap}} H^\circ_{298}(\text{H}_2\text{O})$, Keenan *et al.*, old steam tab. $1.2 \times 0.002 \text{ kcal/mol}$

ATcT HYPOTHESIS TEST (“WHAT IF”)



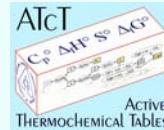
ATcT

- **Hypothesis:** all photoionization experiments are off:
→ all $\Delta E_0(\text{OH}^+/\text{H}_2\text{O})$ increased by 23.8 cm^{-1}
- Statistical analysis points to the following “optimistic” uncertainties:
 - $D_0(\text{OH})$, Carbone & Dalby $11.2 \times 15 \text{ cm}^{-1}$
 - $D_0(\text{H-OH})$, Harich et al. $4.1 \times 5 \text{ cm}^{-1}$
 - $\Delta E_0(\text{OH}^+/\text{H}_2\text{O})$, PFI-PE Berkeley $1.5 \times 0.002 \text{ eV}$
 - $\Delta_{\text{vap}}H^\circ_{298}(\text{H}_2\text{O}_2)$, Edgerton et al. 2nd Law $1.4 \times 0.74 \text{ kcal/mol}$
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 - $\Delta_{\text{vap}}H^\circ_{298}(\text{H}_2\text{O})$, Keenan et al., old steam tab. $1.2 \times 0.002 \text{ kcal/mol}$
 - $\Delta_{\text{vap}}H^\circ_{298}(\text{H}_2\text{O}_2)$, Edgerton et al. 3rd Law $1.1 \times 0.038 \text{ kcal/mol}$
- $\Delta H_f^\circ(\text{OH}) = 8.86_3 \pm 0.00_9 \text{ kcal/mol}$
(cf. unbiased ATcT $8.85_9 \pm 0.01_7 \text{ kcal/mol}$) X
- $D_0(\text{H-OH}) = 41130 \pm 4 \text{ cm}^{-1}$
(cf. unbiased ATcT $41129 \pm 7 \text{ cm}^{-1}$)
- $D_0(\text{OH}) = 35588 \pm 6 \text{ cm}^{-1}$
(cf. unbiased ATcT $35590 \pm 12 \text{ cm}^{-1}$)

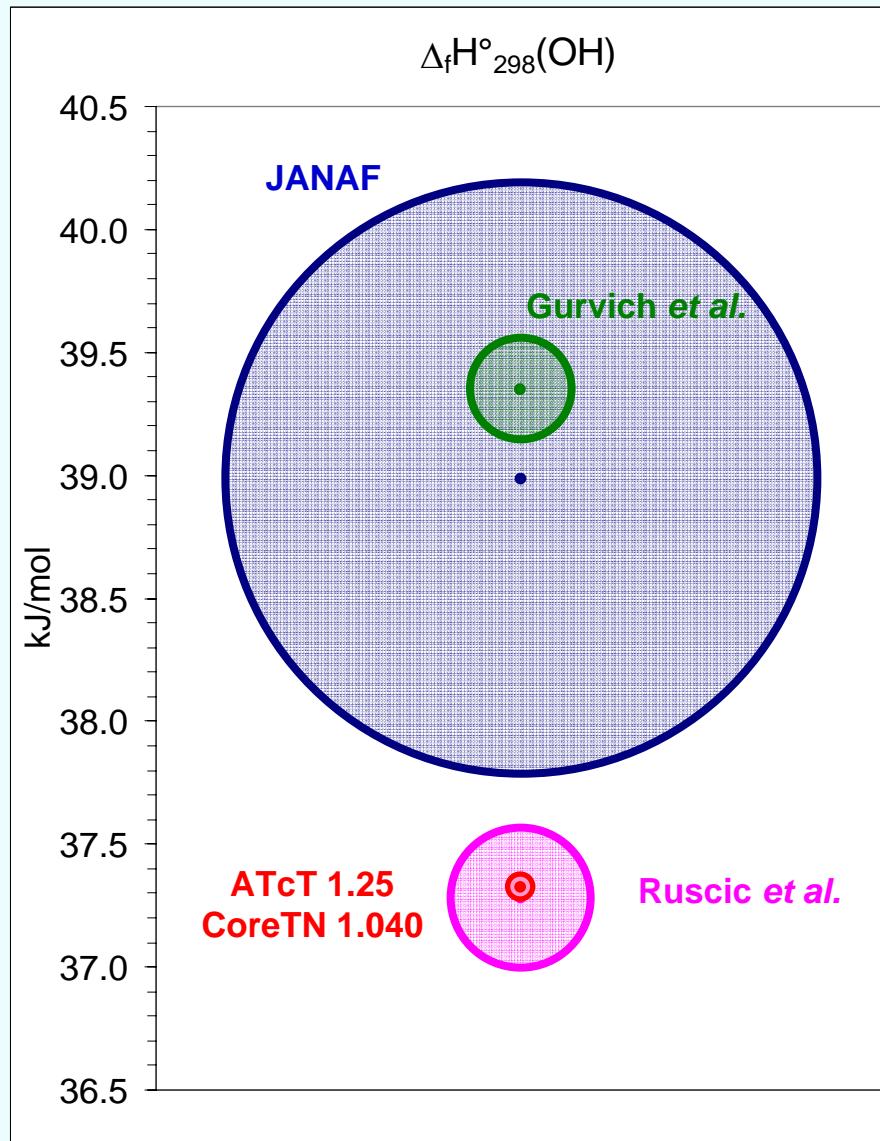


Though the network does not allow the values to stray away too much, this solution has to be rejected because it's based on a hypothesis demonstrated to be incorrect

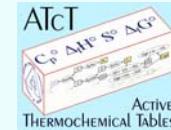
BOTTOM LINE...



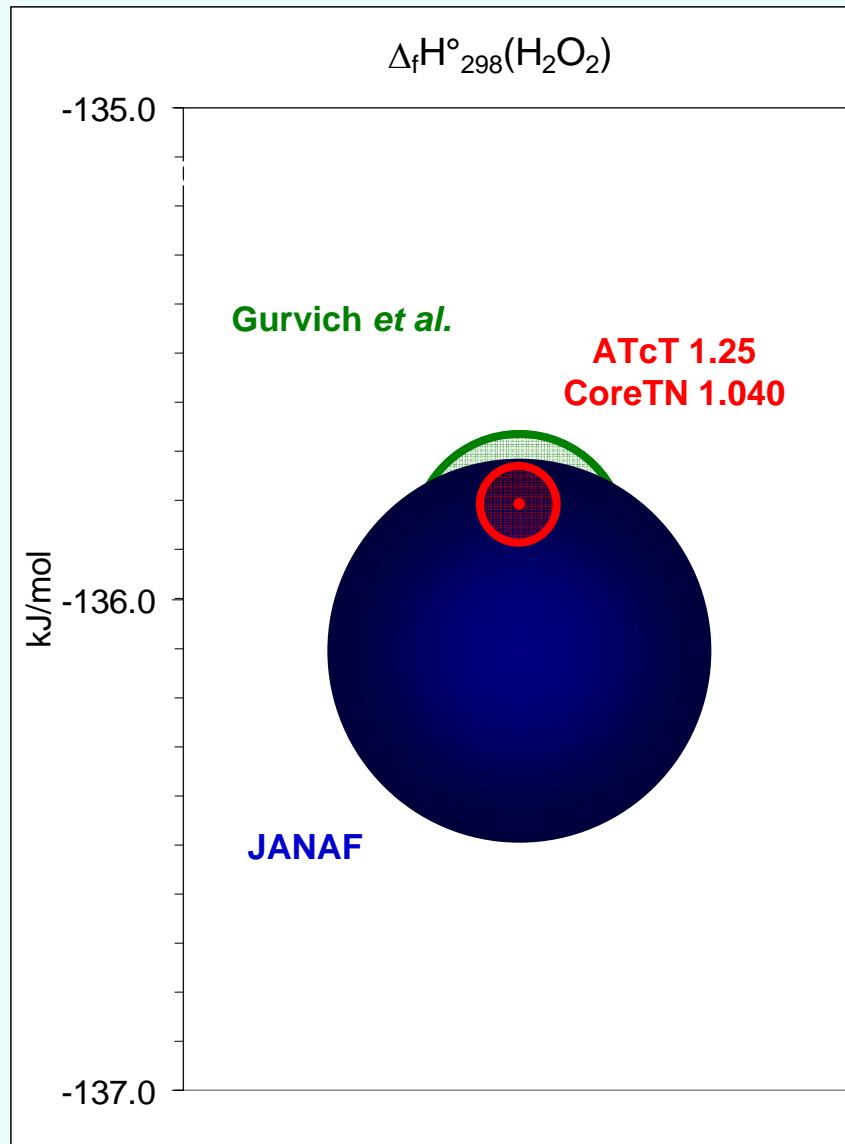
ATcT



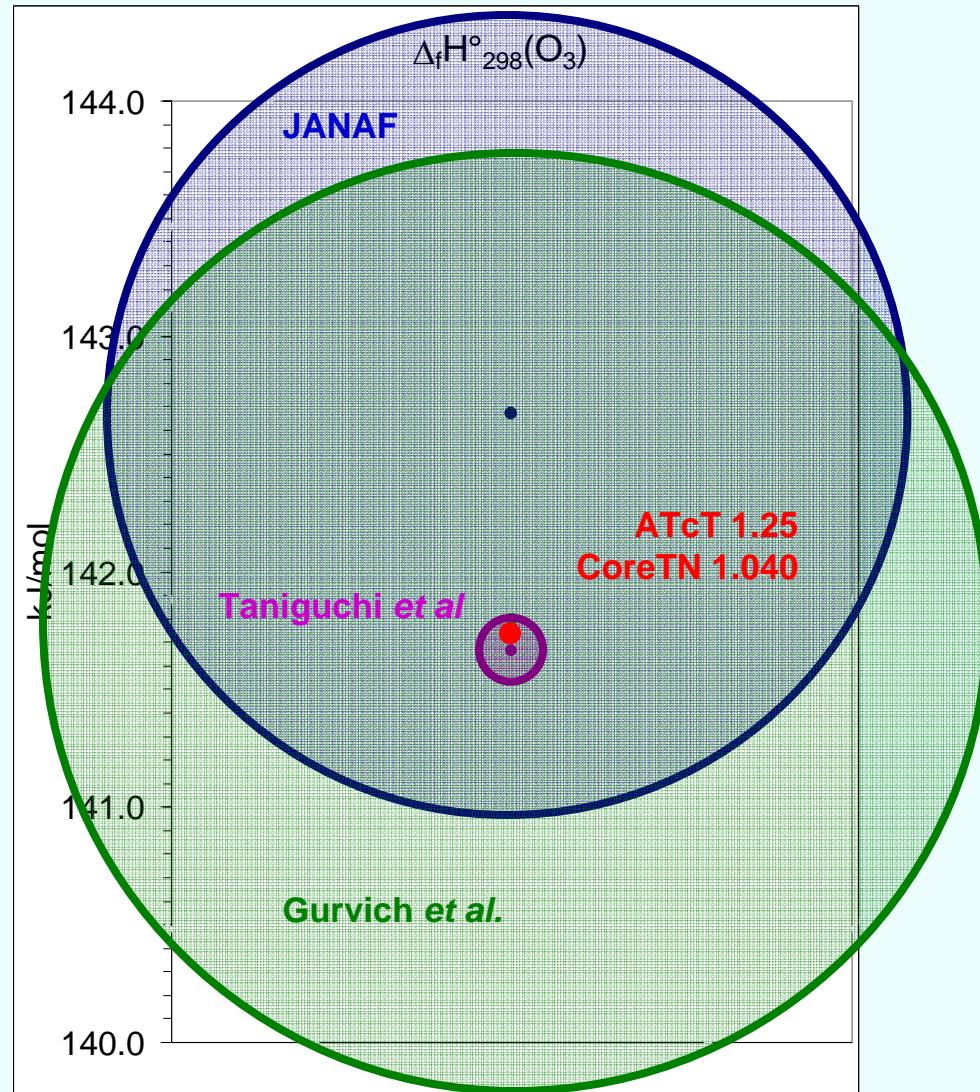
A few corollaries...H₂O₂



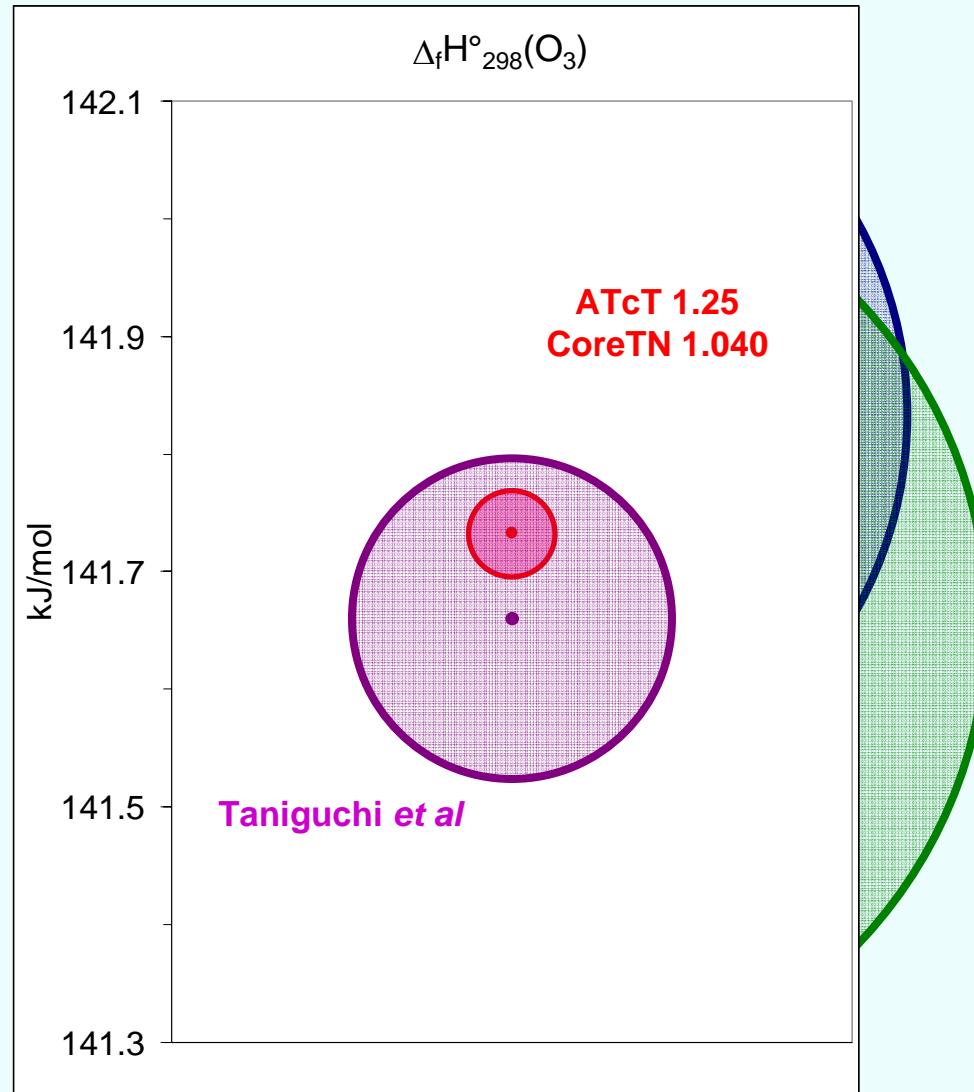
ATcT



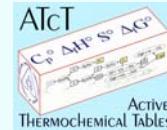
A few corollaries... O₃



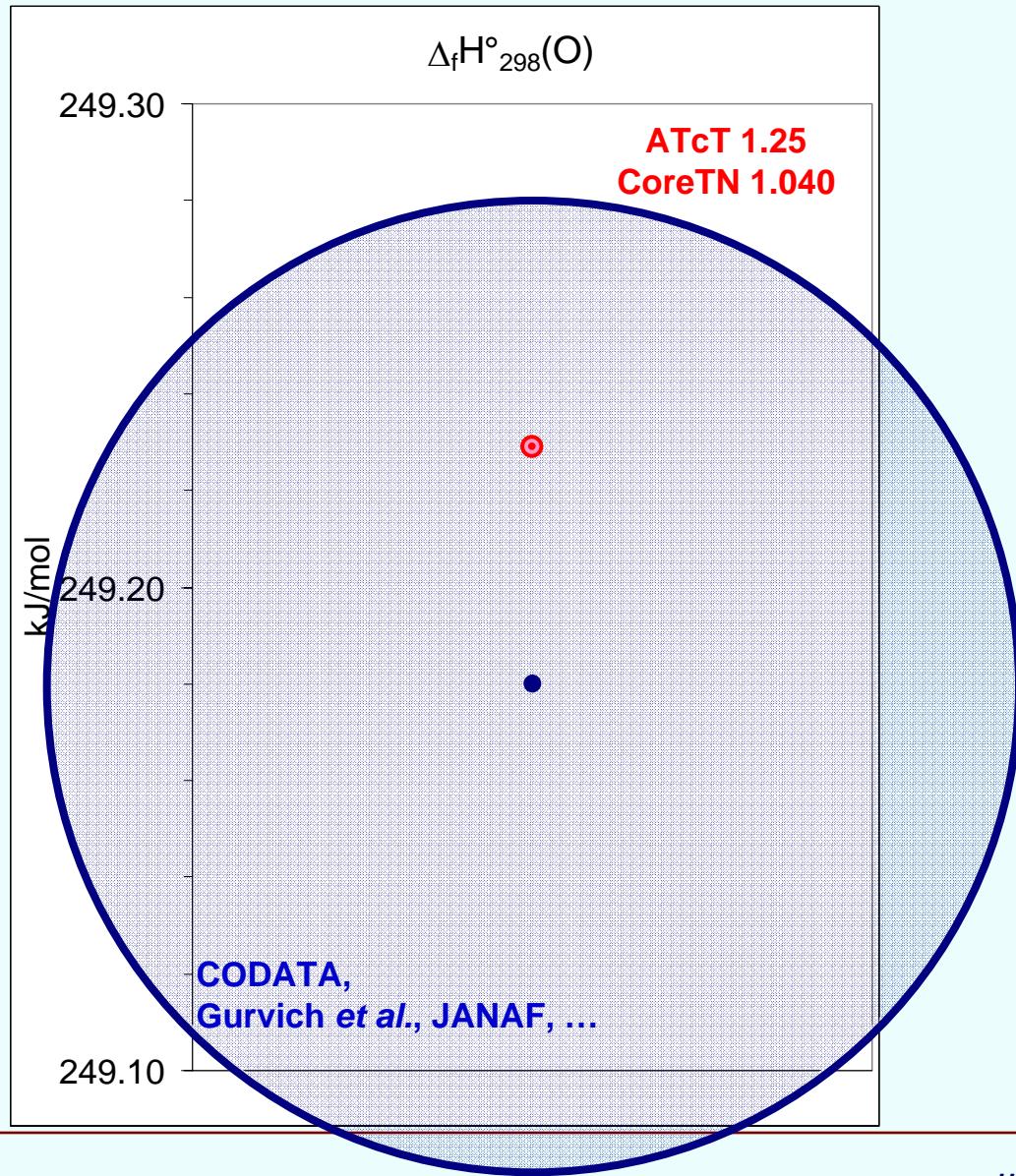
A few corollaries... O₃



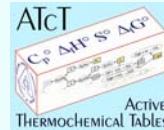
A few corollaries... O



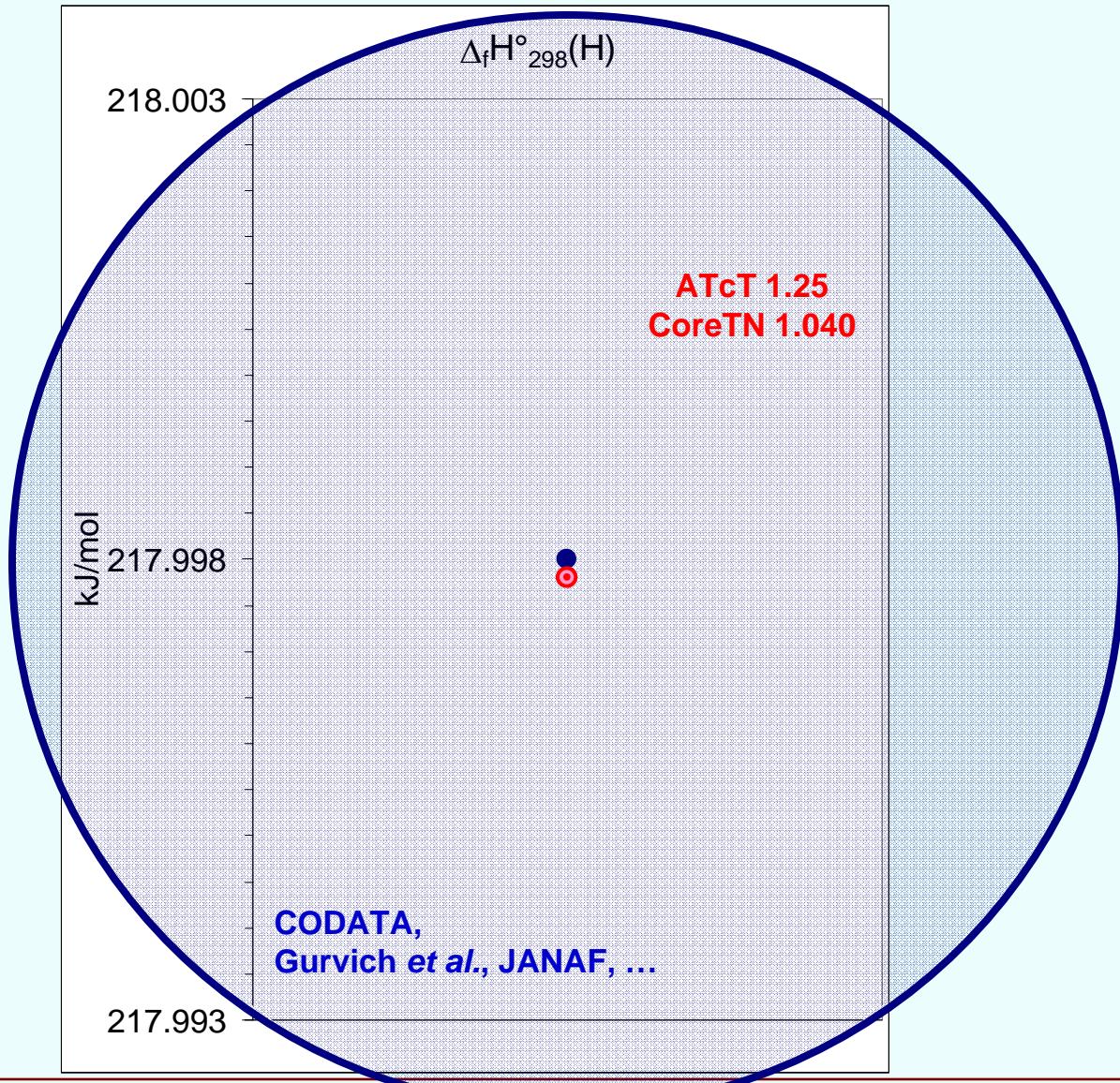
ATcT

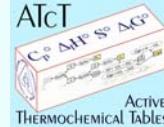


A few corollaries... H



ATcT





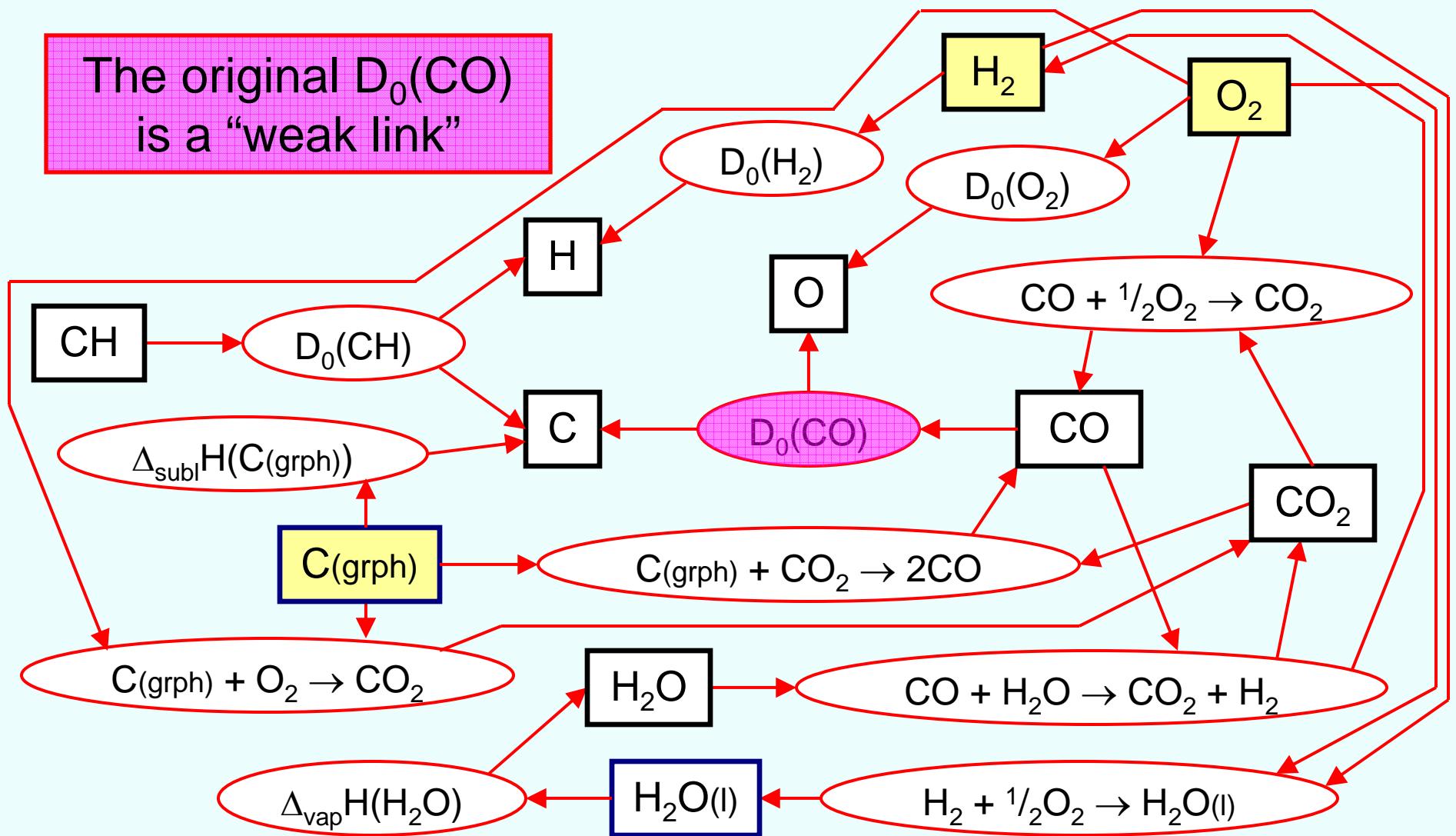
ATcT

THE C (g) QUESTION

- It's a 50-year old puzzle...
- $\Delta_f H^\circ(C(\text{gas})) \equiv \Delta_{\text{subl}} H^\circ(C(\text{graphite}))$
- $\Delta_f H^\circ(C(\text{gas}))$ is one of the CODATA “key” thermochemical quantities
- *Inter alia*, it is used as a fixed reference point for carbon by all *ab initio* computations (such as Gn , Wn , etc) that produce enthalpies of formation via atomization energies
- Early measurements attempted to determine $\Delta_{\text{subl}} H^\circ(C(\text{graphite}))$ via measurements of equilibria
- CODATA used $D_0(\text{CO})$, once it got settled...

THE C (g) QUESTION

The original $D_0(\text{CO})$
is a “weak link”



THE D₀(CO) QUESTION

- A. E. Douglas and C. K. Moller, *Can. J. Phys.* **33**, 125 (1955)

PREDISSOCIATIONS OF THE C¹²O AND C¹³O MOLECULES¹

By A. E. DOUGLAS AND C. K. MØLLER²

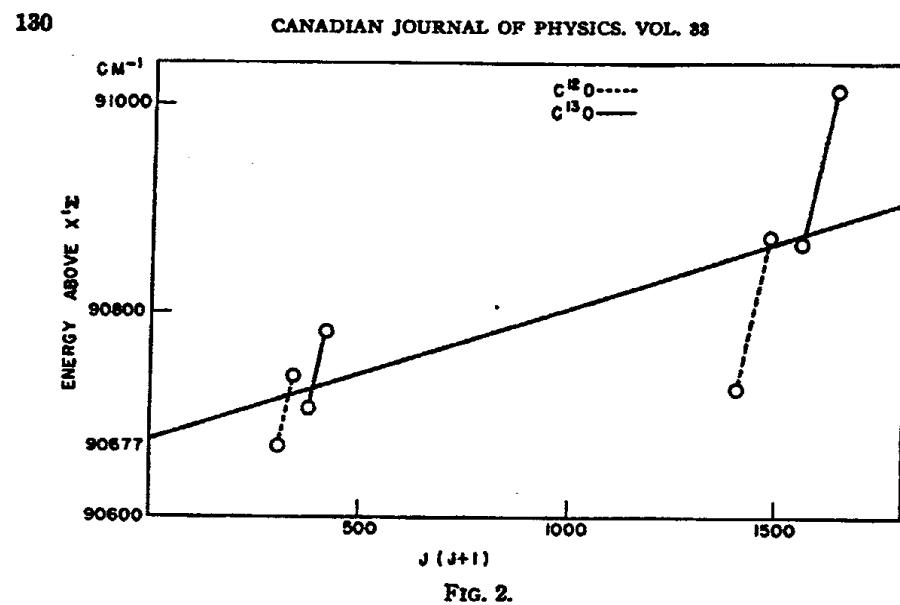
ABSTRACT

The Ångström bands of C¹²O and C¹³O have been photographed with a high dispersion spectrograph and the predissociations previously reported in these bands have been re-examined. The predissociations provide good evidence that C¹²O has a dissociation limit $89595 \pm 30 \text{ cm}^{-1}$ above the $v = 0$ level of the ground state. The fourth positive ($A^1\Pi - X^1\Sigma$) bands have been re-examined and it has been shown that, contrary to earlier reports, there is no evidence for predissociation in the $A^1\Pi$ state.

- The uncertainty addressed at the time was whether D₀(CO) is:
 - ~ 11.1 eV from apparent predissociation at $v' = 0, J > 37$ of the Ångström system of CO ($B^1\Sigma \leftarrow$ of $A^1\Pi$), or
 - ~ 9.6 eV suggested by electron impact and supported by observed weakening of some lines at $v = 7, 8, 9$ in the fourth positive system ($A^1\Pi \leftarrow$ of $X^1\Sigma$) of CO or some yet different value

THE $D_0(\text{CO})$ QUESTION

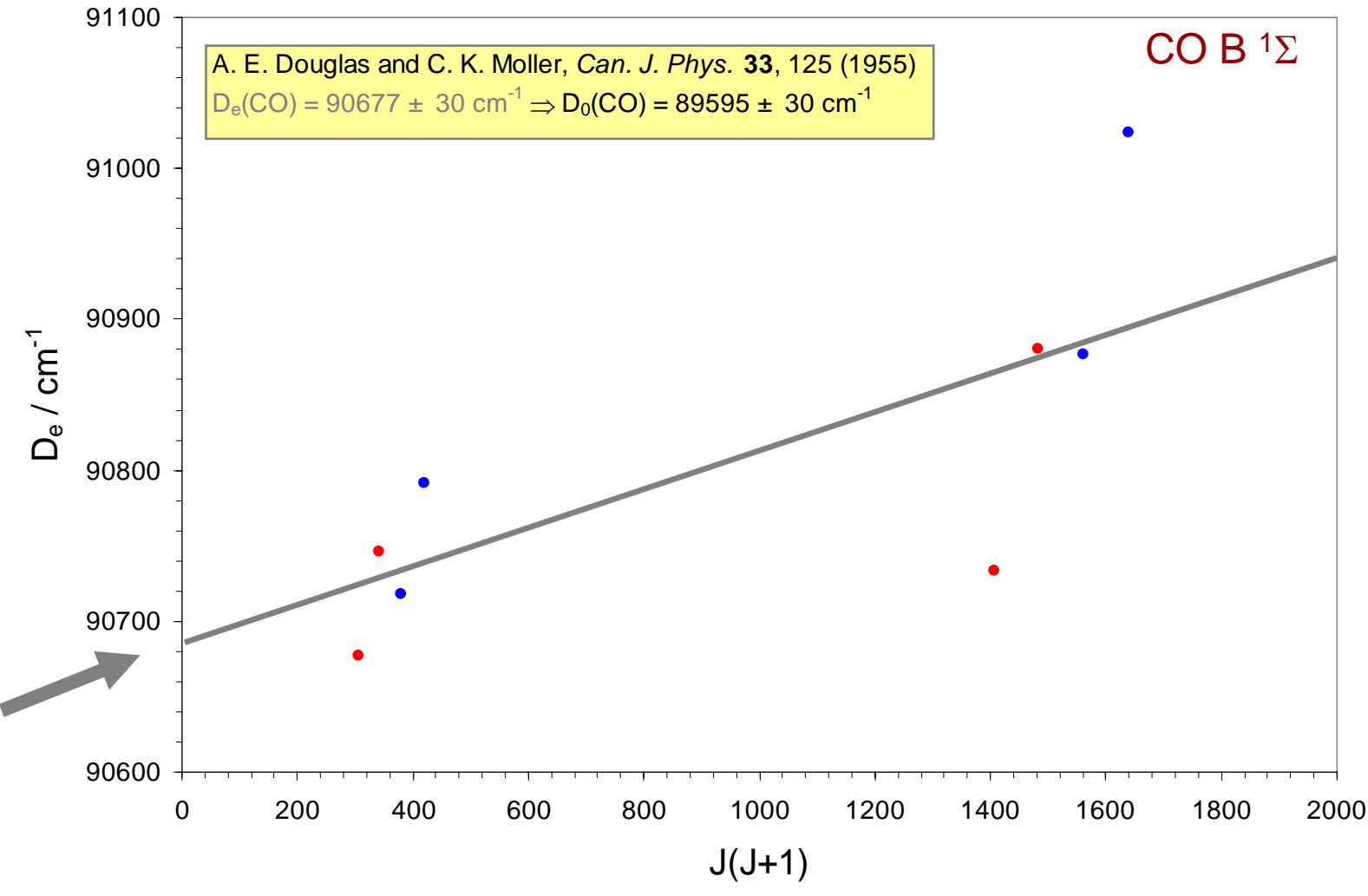
- A. E. Douglas and C. K. Moller, *Can. J. Phys.* **33**, 125 (1955)
- ^{12}CO $\text{B}^1\Sigma$ predissociation clearly observed between $J = 37$ and 38 in $v = 0$
 ^{13}CO $\text{B}^1\Sigma$ predissociation clearly observed between $J = 17$ and 18 in $v = 1$
- ^{12}CO $\text{B}^1\Sigma$ predissociation clearly observed between $J = 39$ and 40 in $v = 0$
 ^{13}CO $\text{B}^1\Sigma$ predissociation clearly observed between $J = 19$ and 20 in $v = 1$



$$D_0(\text{CO}) = 89595 \pm 30 \text{ cm}^{-1}$$

LIMITING CURVES OF DISSOCIATION of CO

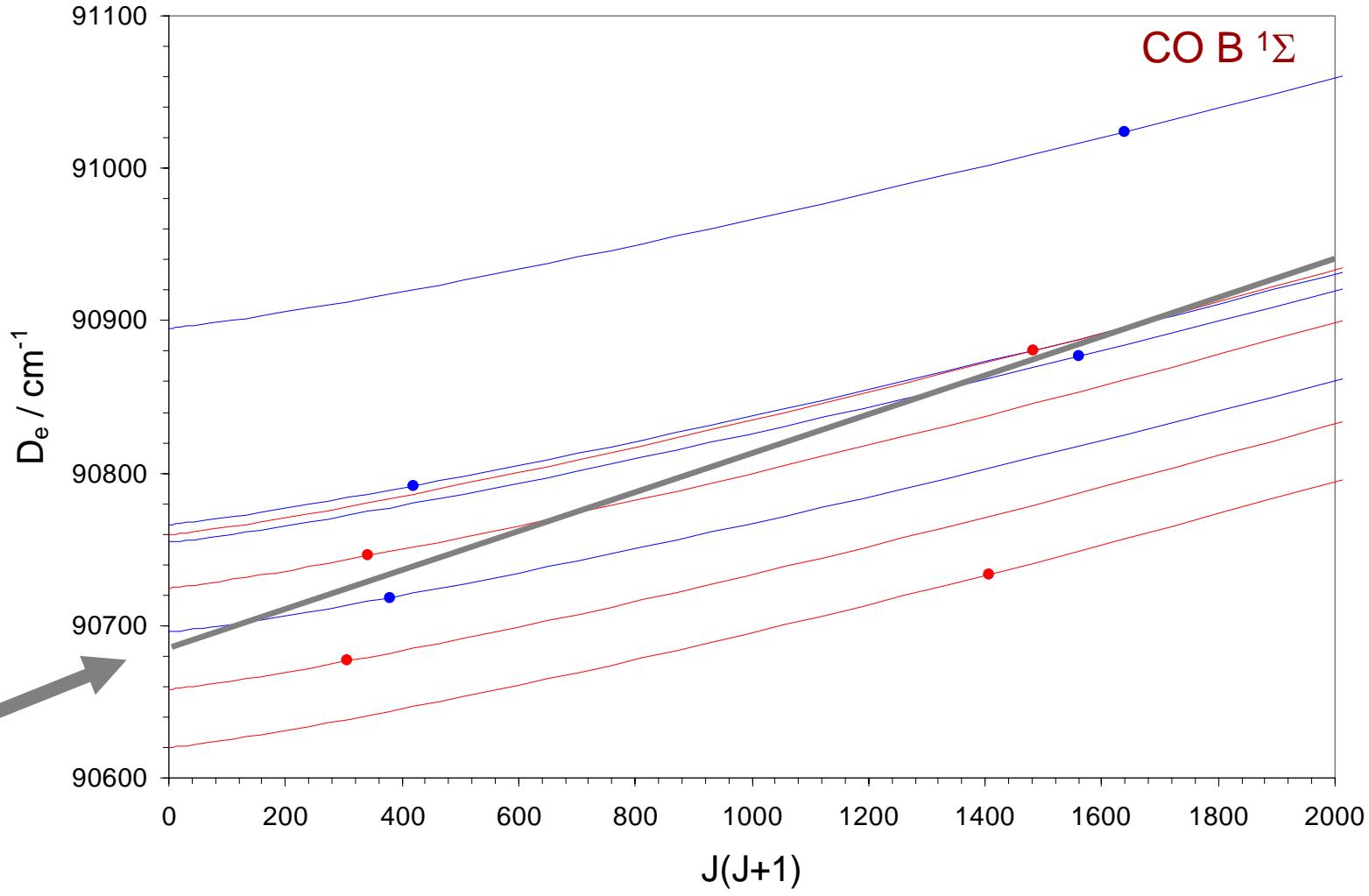
$^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ - Limiting Curves of Dissociation



LIMITING CURVES OF DISSOCIATION of CO

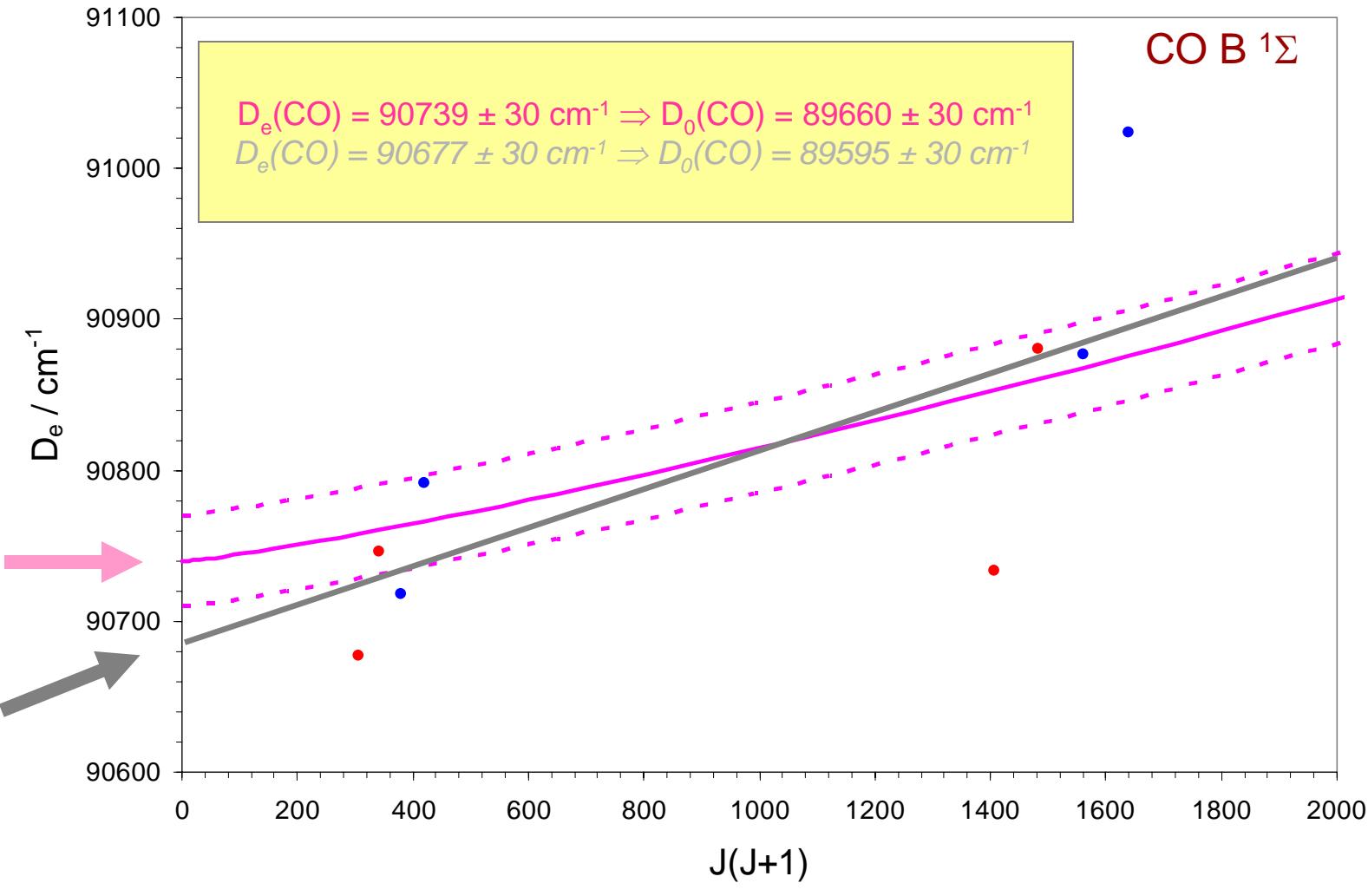
ATcT

¹²C¹⁶O and ¹³C¹⁶O - Limiting Curves of Dissociation



LIMITING CURVES OF DISSOCIATION of CO

$^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ - Limiting Curves of Dissociation



D₀(CO)

ATcT

- From reinterpretation of spectroscopic data:

~~$$D_e(\text{CO}) = 90677 \pm 30 \text{ cm}^{-1} \Rightarrow D_0(\text{CO}) = 89595 \pm 30 \text{ cm}^{-1}$$~~

$$D_e(\text{CO}) = 90739 \pm 30 \text{ cm}^{-1} \Rightarrow D_0(\text{CO}) = 89660 \pm 30 \text{ cm}^{-1}$$

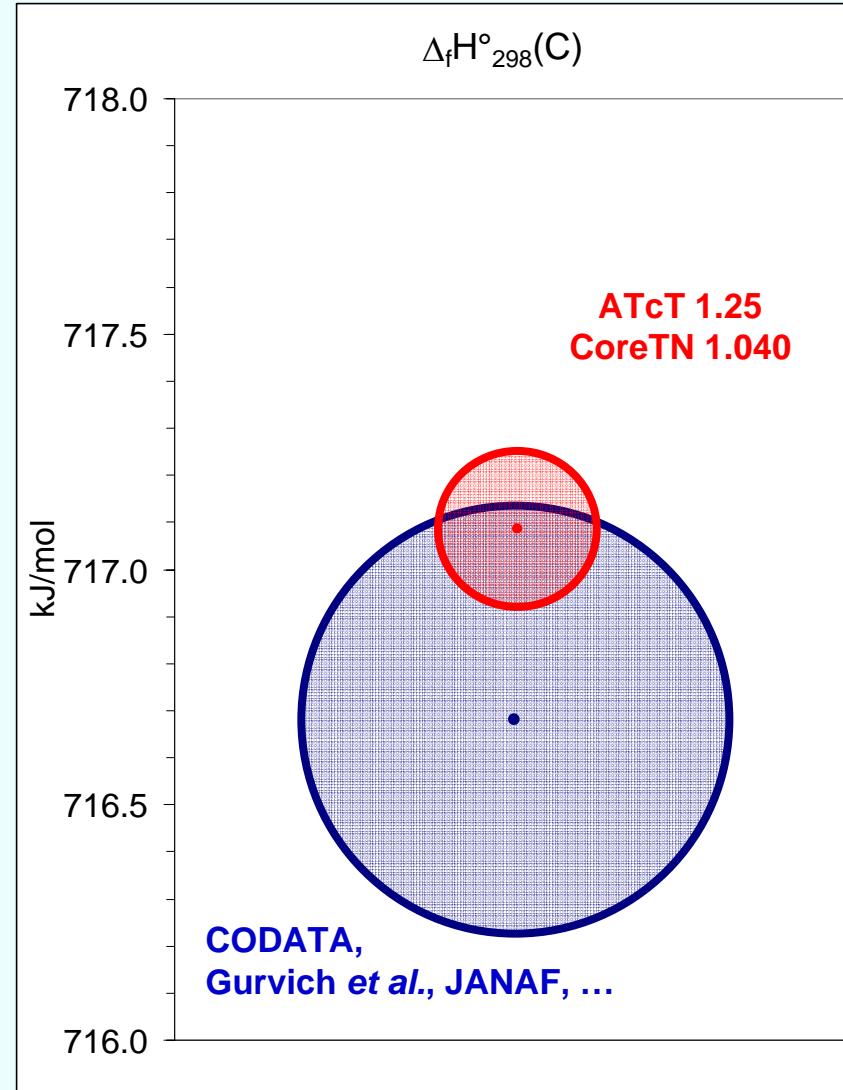
(uncert. reflects a slight discrepancy between ¹²CO and ¹³CO)

- Best estimate from state of the art ab initio calculations:
(using converged levels of var. methods, including higher order coupled cluster and full configuration interaction benchmarks extrapolated to complete basis set full configuration interaction limit plus corrections for relativistic effects and diagonal Born-Oppenheimer correction to reduce remaining computational errors):

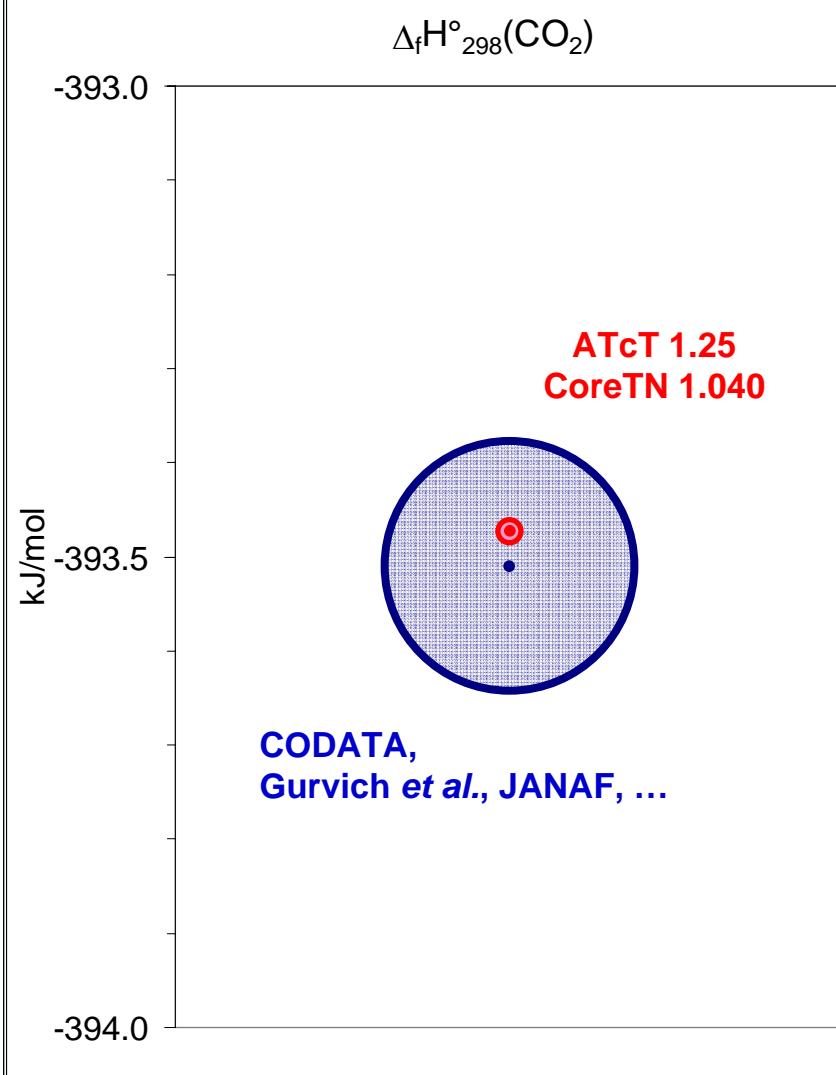
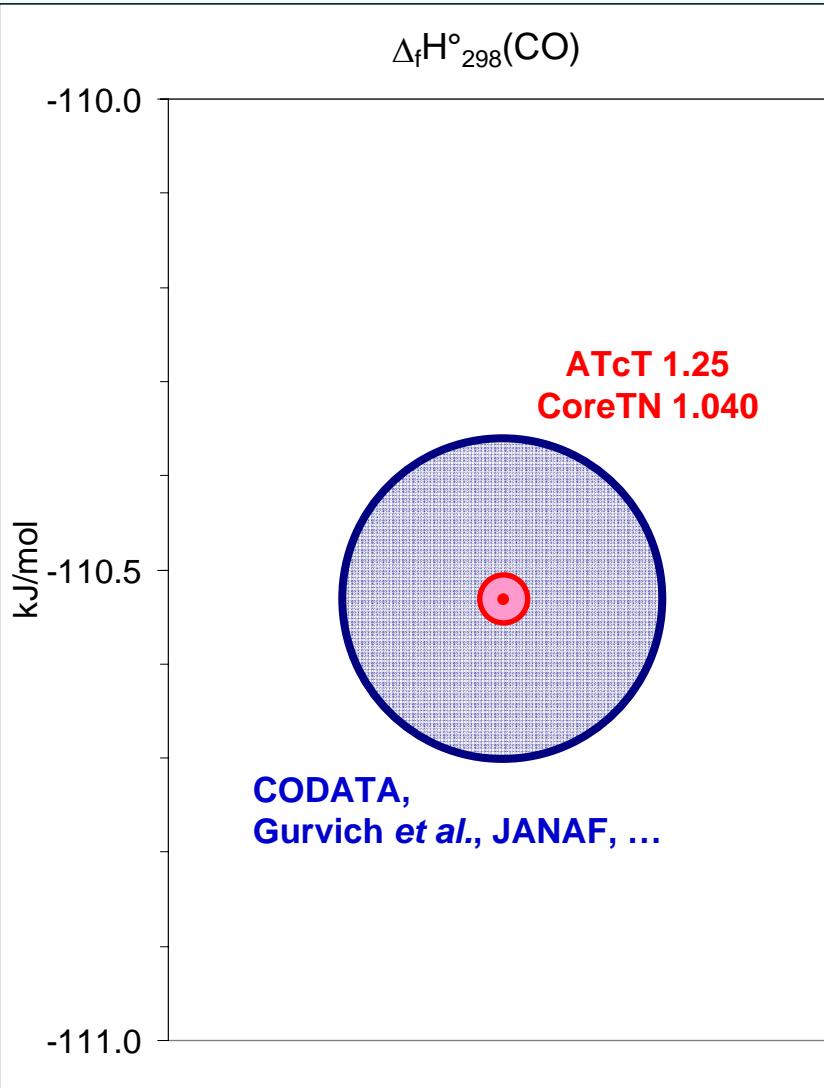
$$D_e(\text{CO}) = 90758 \pm 30 \text{ cm}^{-1} \Rightarrow D_0(\text{CO}) = 89679 \pm 30 \text{ cm}^{-1}$$

- We are currently pursuing additional experiments at ALS in collaboration with C.-Y. Ng (measurements are in progress)

THE C (g) QUESTION



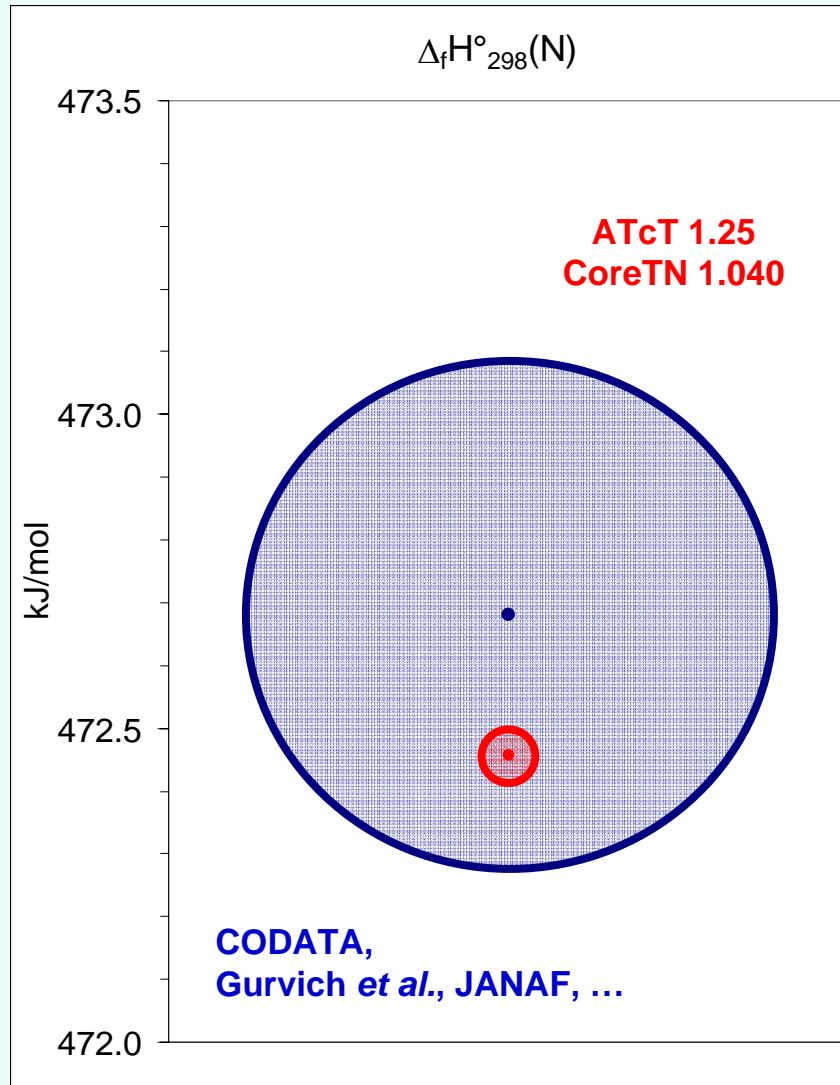
A couple of corollaries...



N



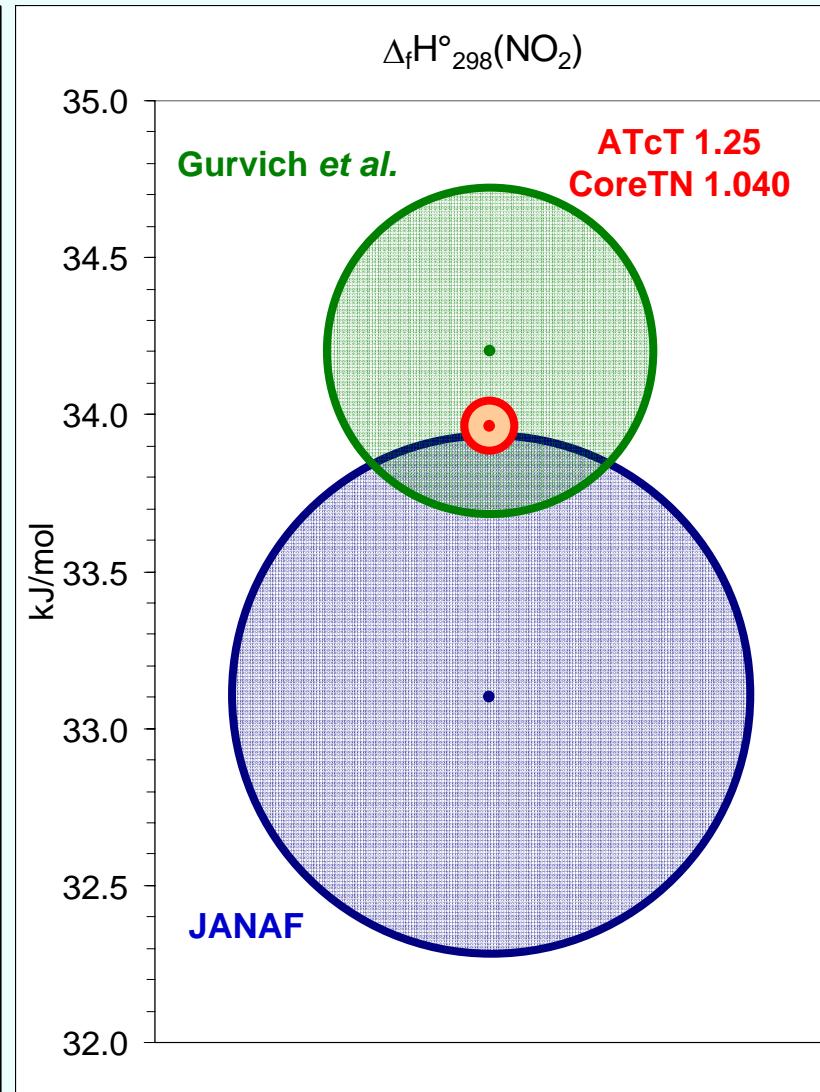
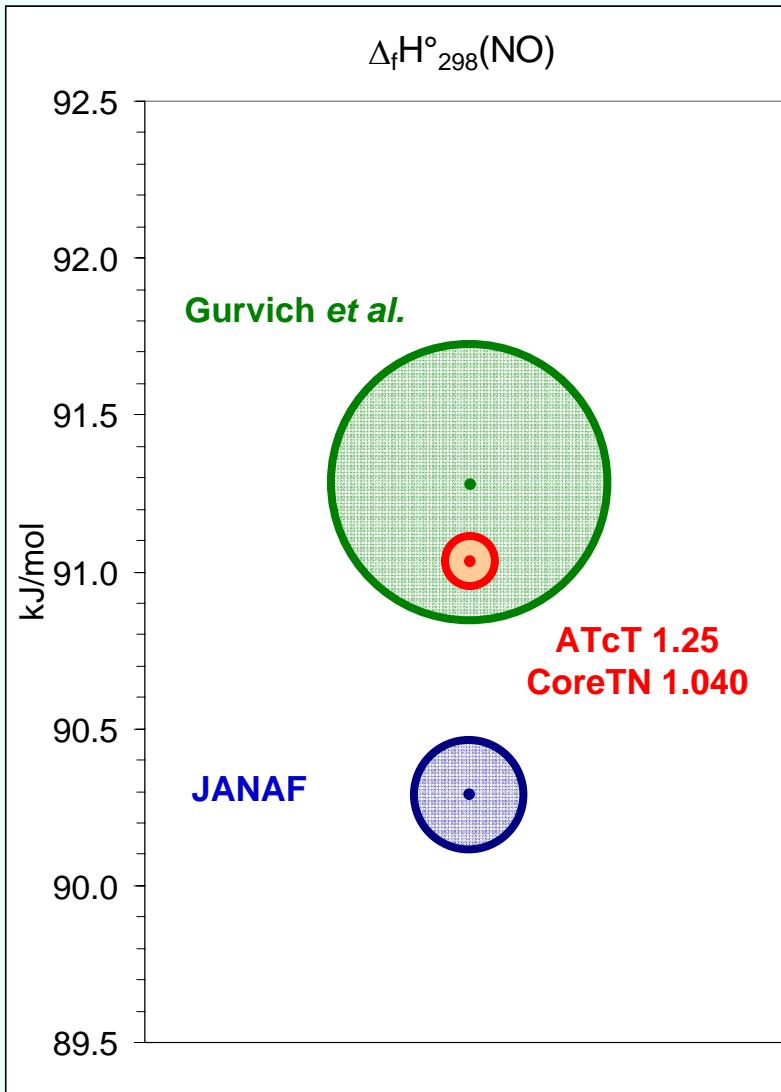
ATcT



$D_0(N_2)$,
the primary
determination
leading to $\Delta_f H^\circ(N)$,
is a
“weak link”
limiting
the accuracy
of the
thermochemistry
of N
and through it of
NO_x species,
as well as many
other
N-containing
species

NO AND NO₂

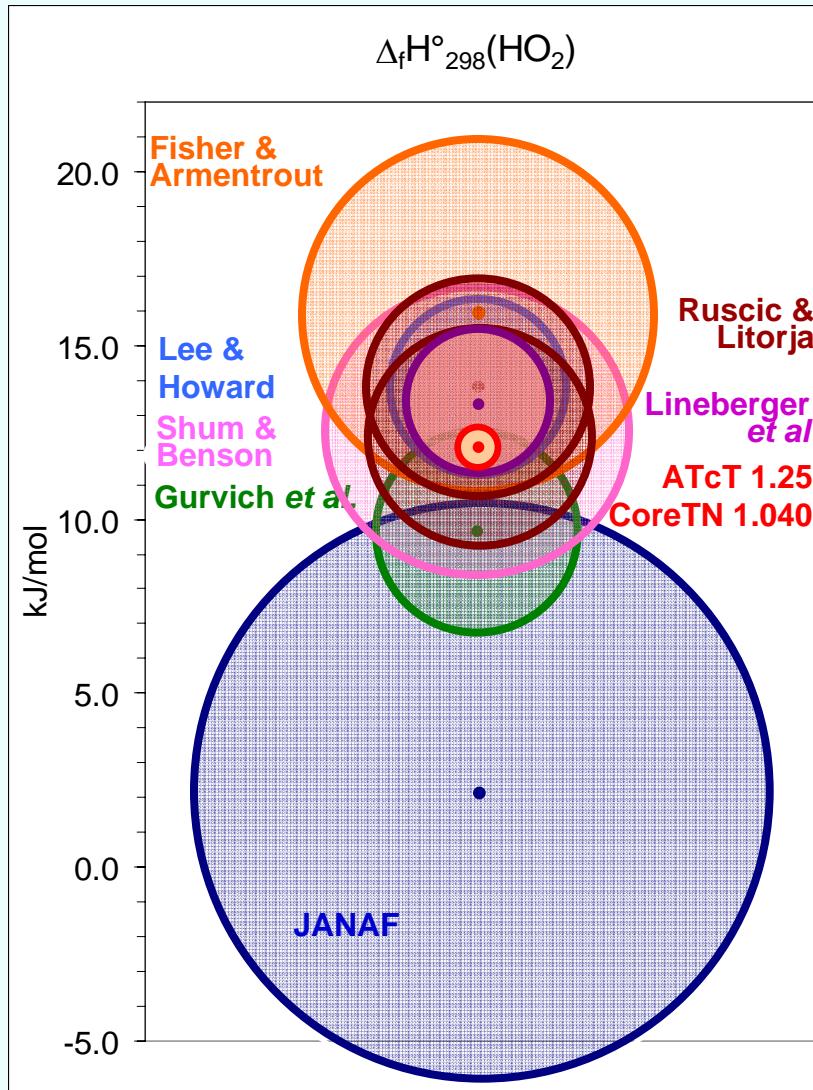
ATcT



HO_2



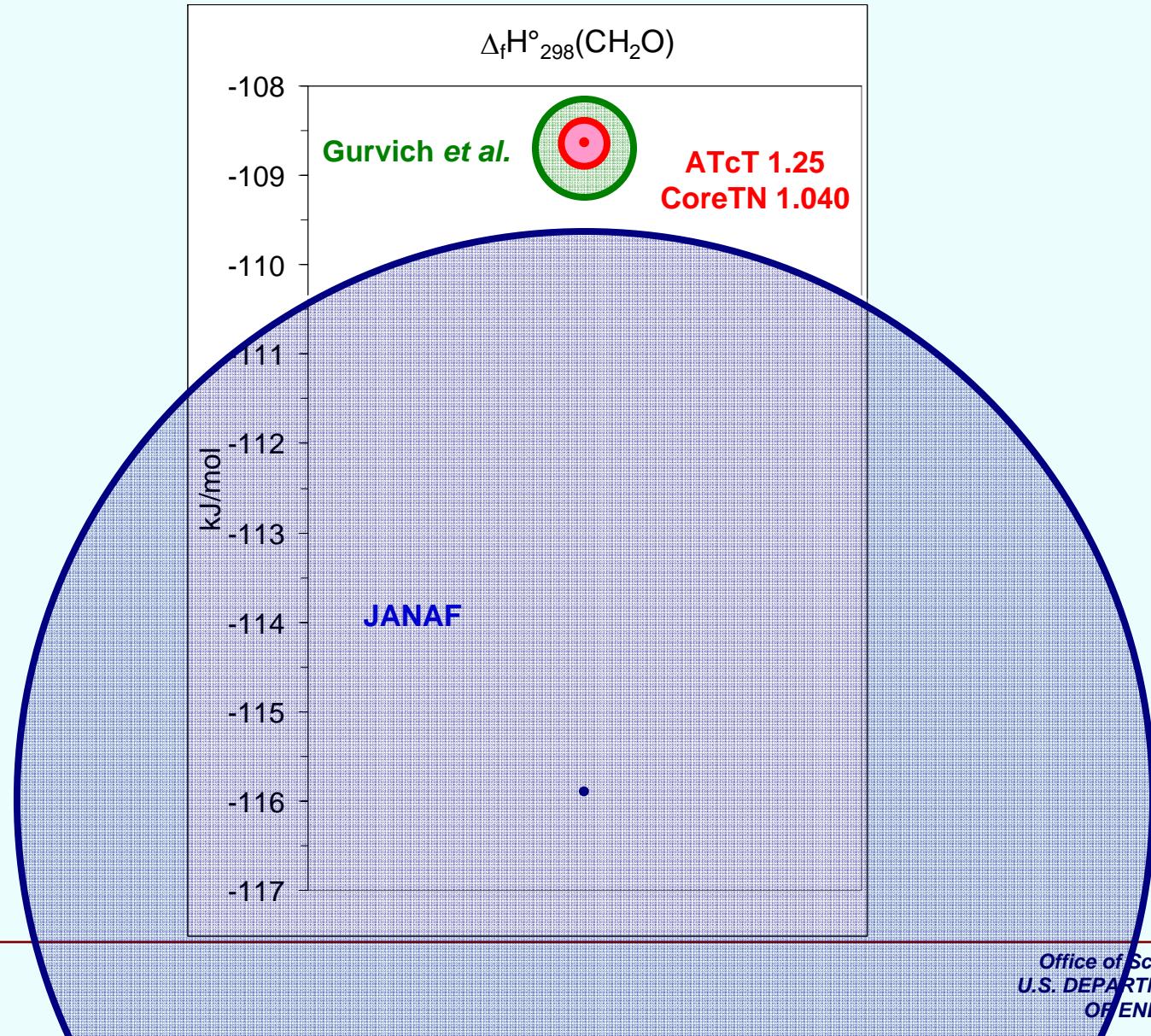
ATcT



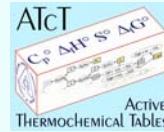
“Howard reaction”
 $\text{OH} + \text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}$

ATcT thermo
+ new kinetic experiments
(J. Michael, ANL):
the reverse rate
was indeed off by
a factor of 2!

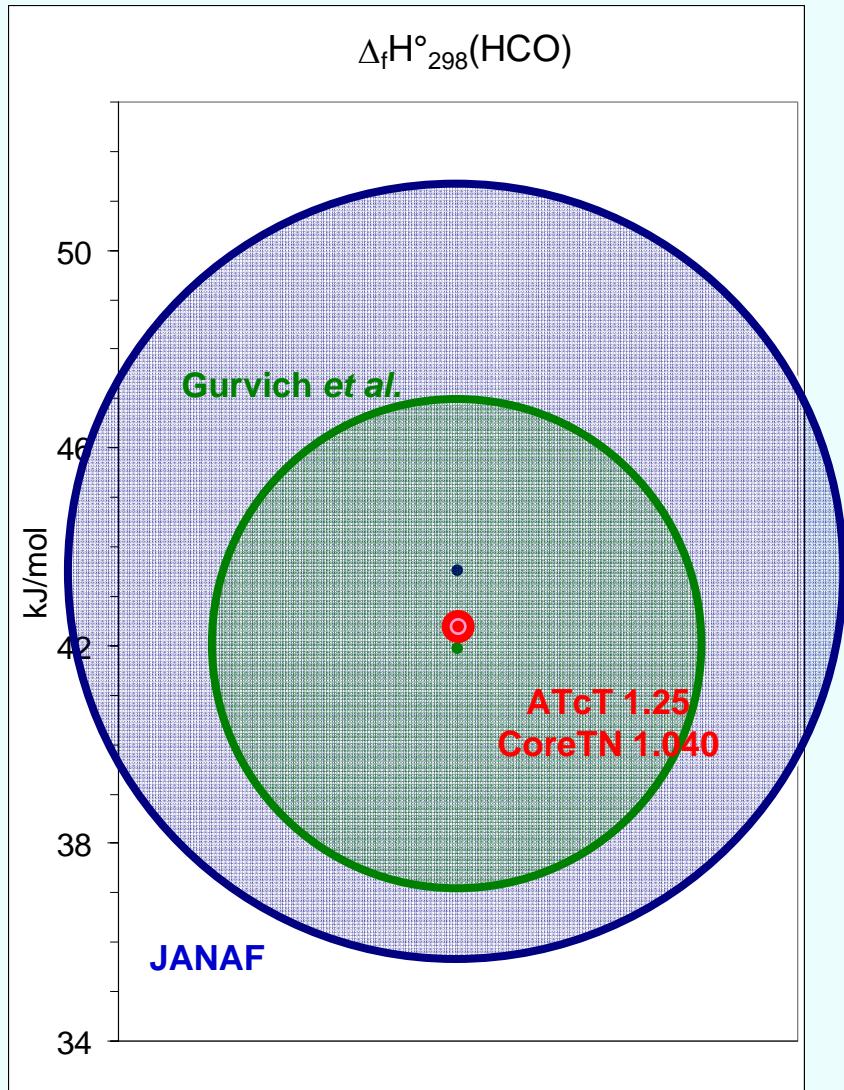
CH₂O



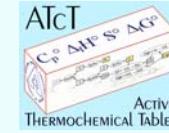
HCO



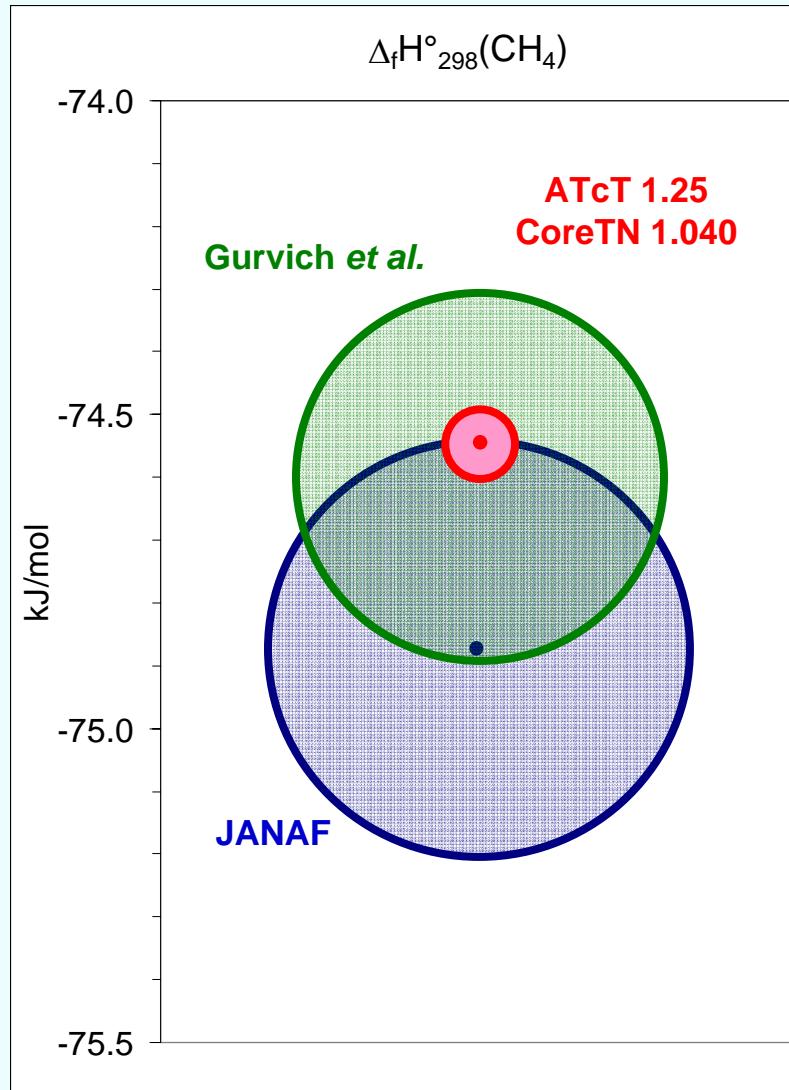
ATcT

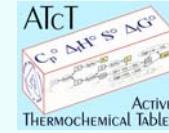


CH₄

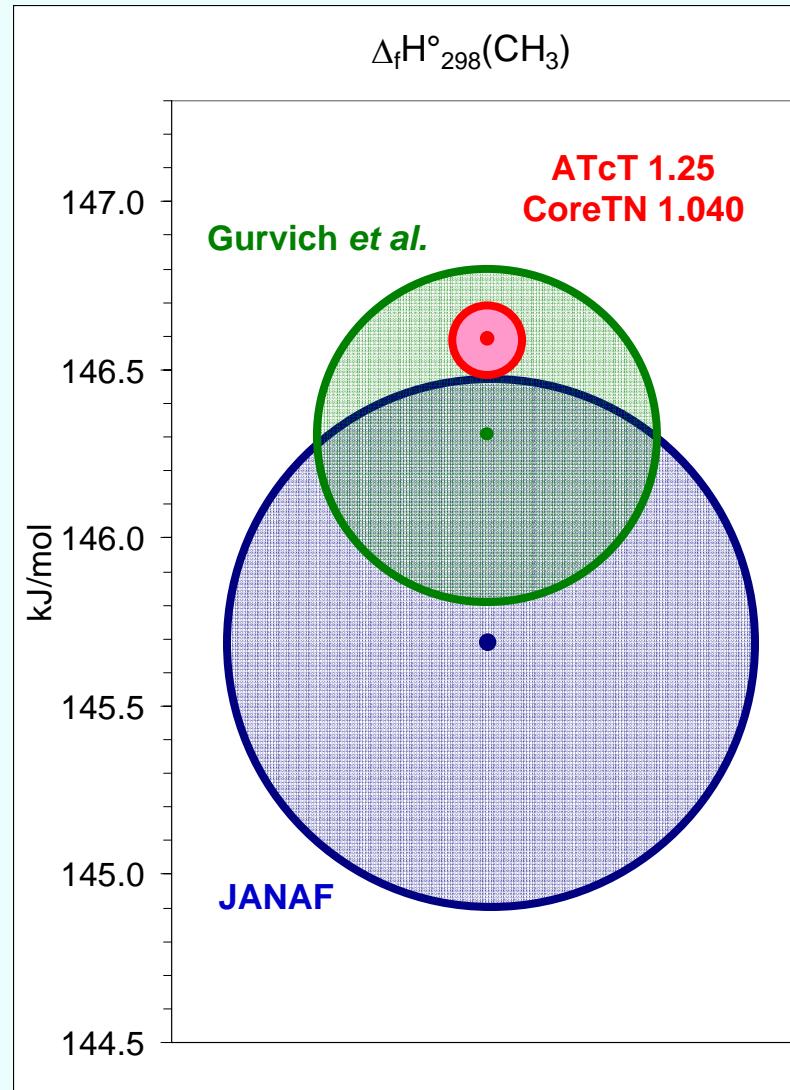


ATcT

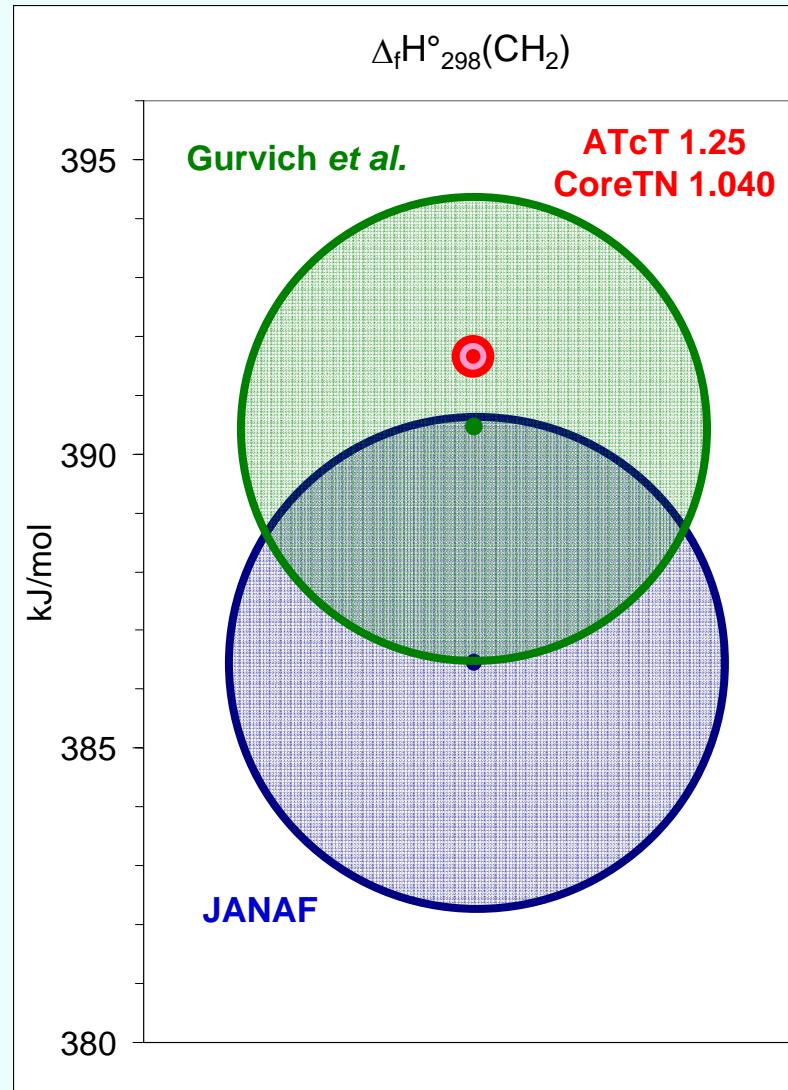




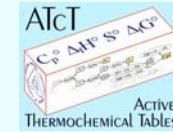
ATcT



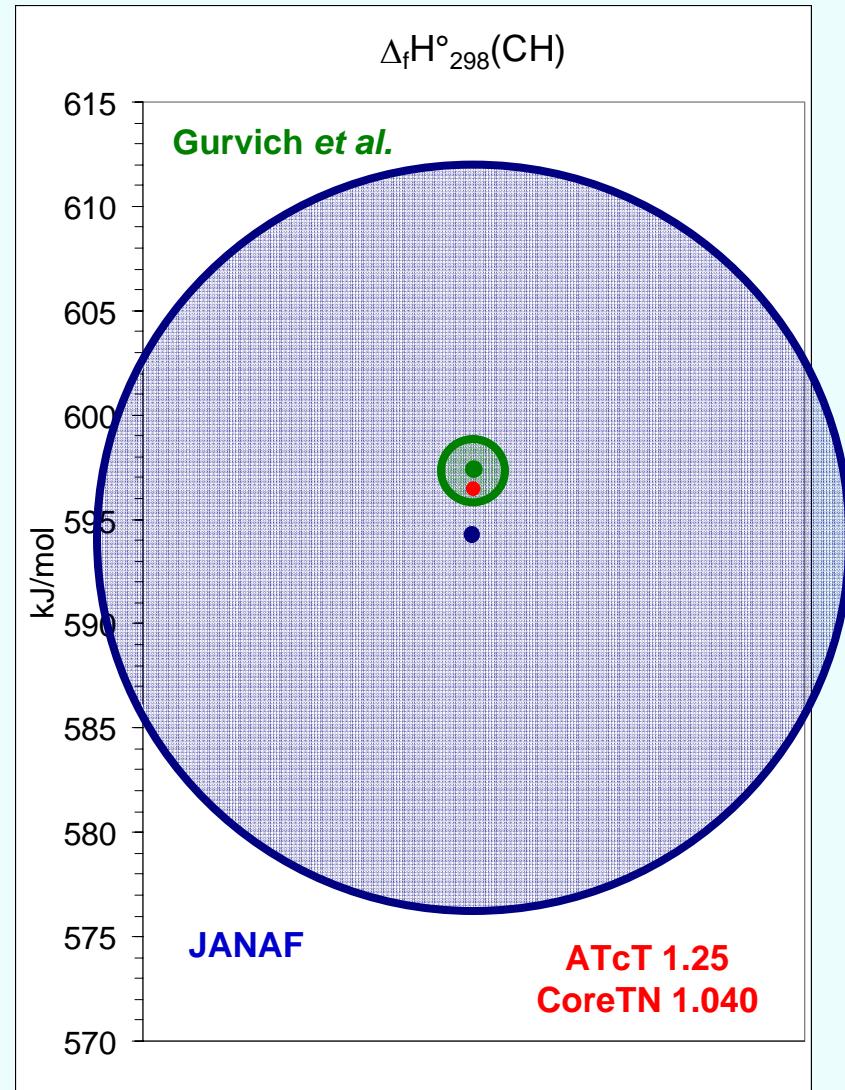
CH₂



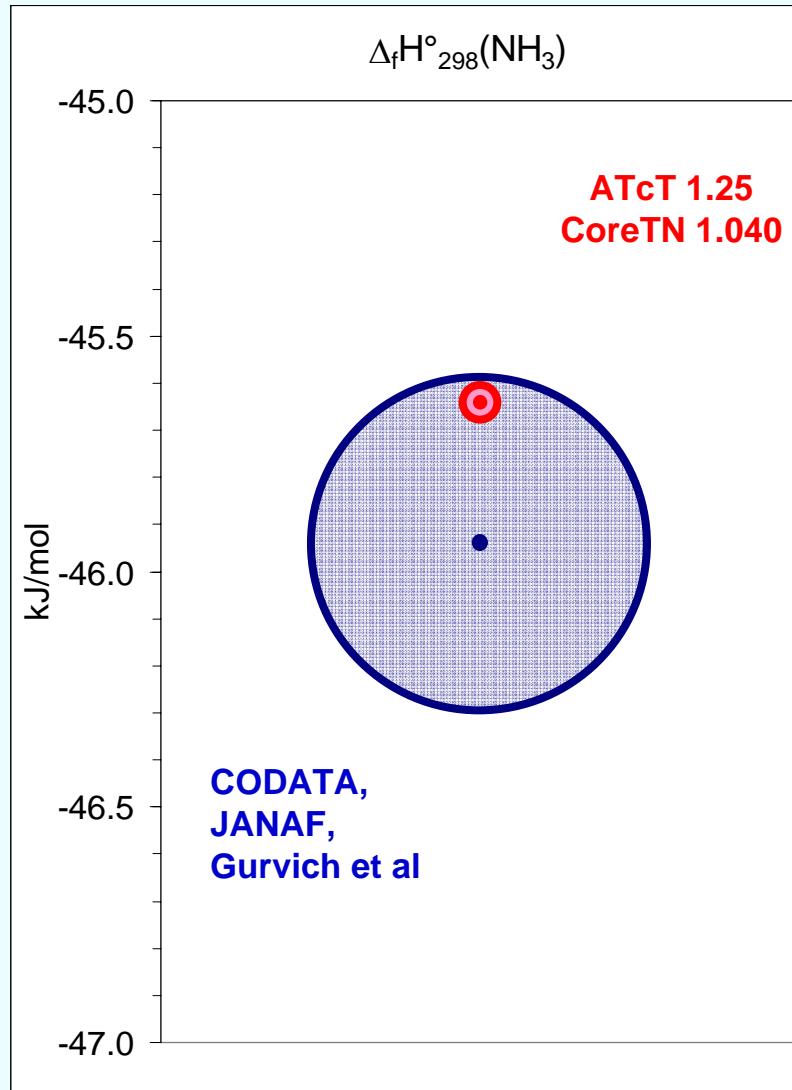
CH



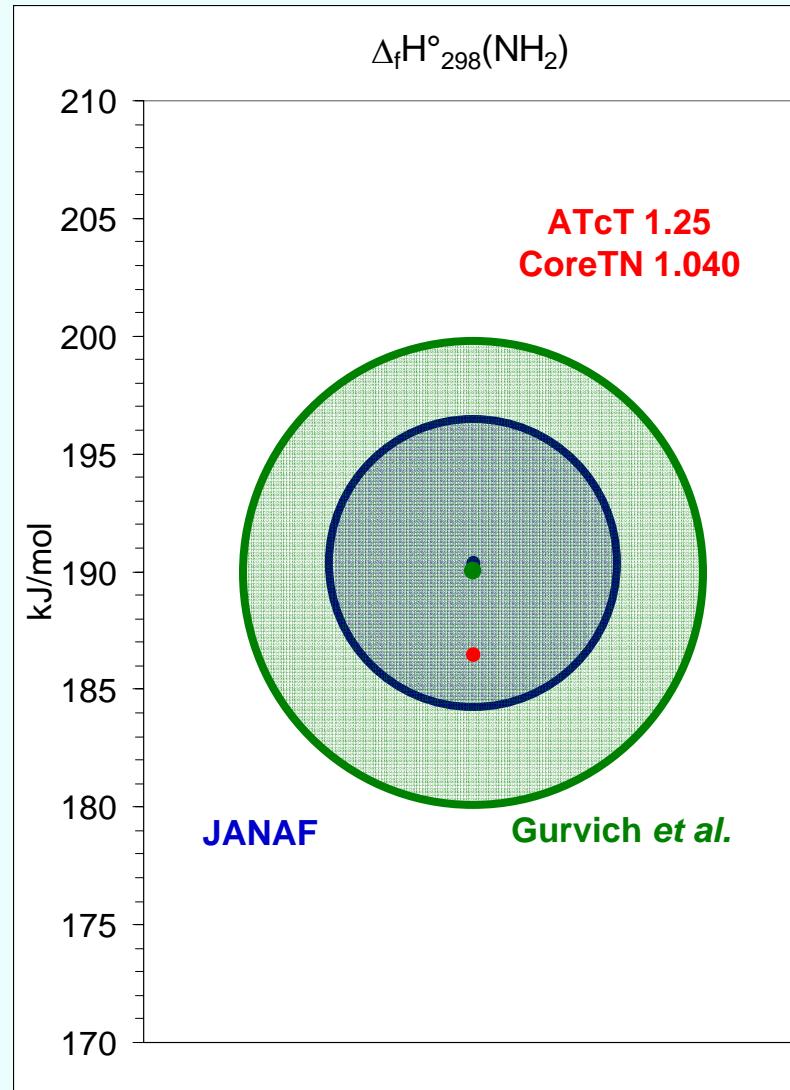
ATcT



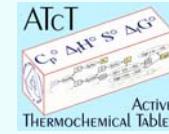
NH₃



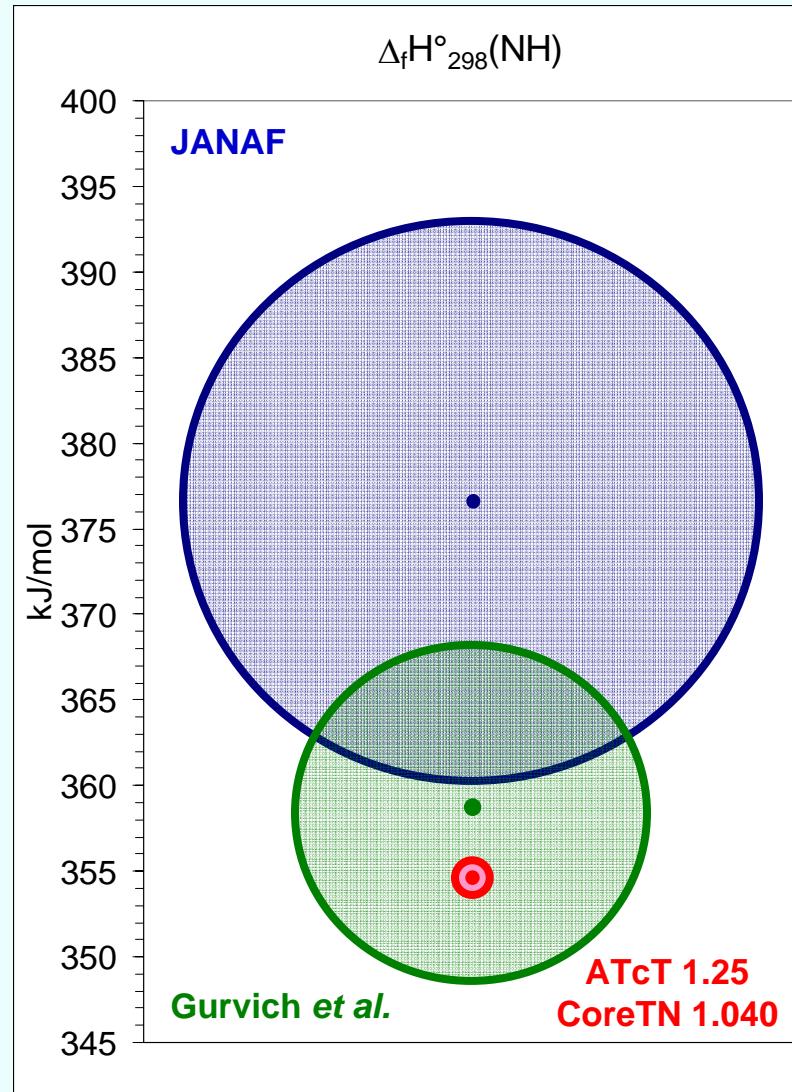
NH₂



NH



ATcT

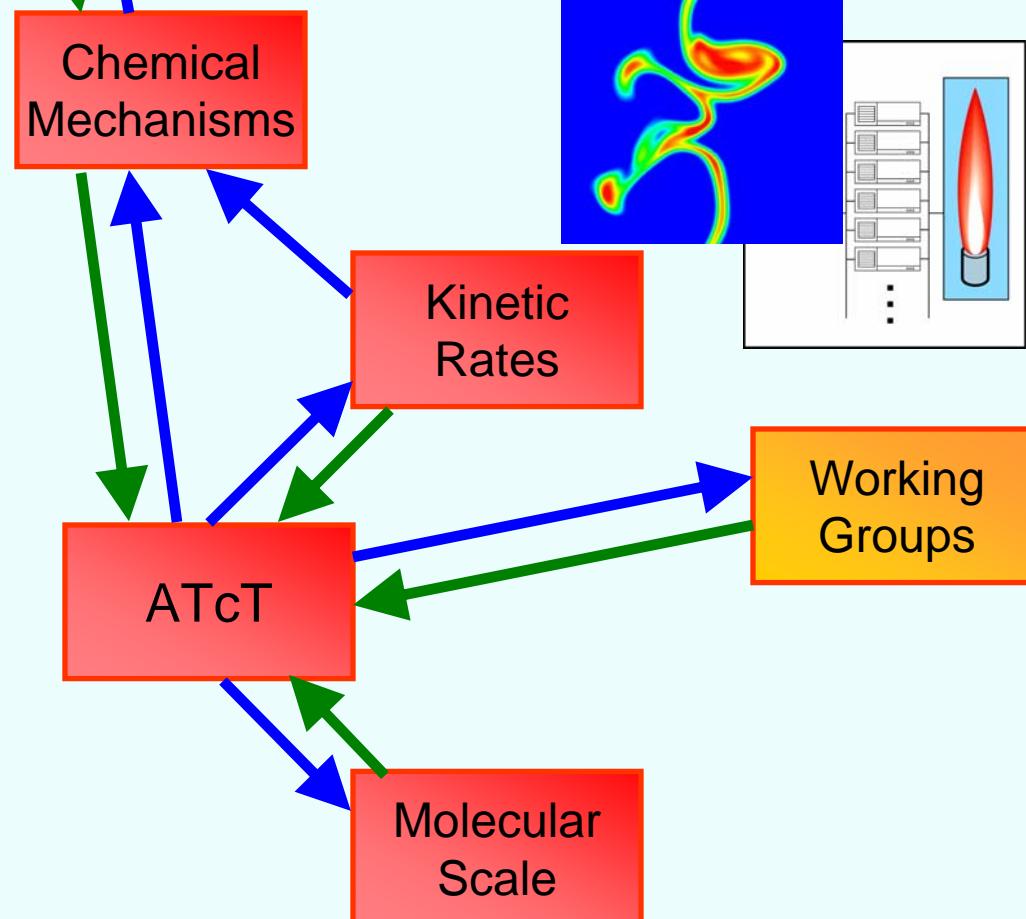




Interplay of ATcT with Multi-Scale Chemical Science

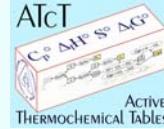


ATcT



- ATcT are a **provider** of information to other scales

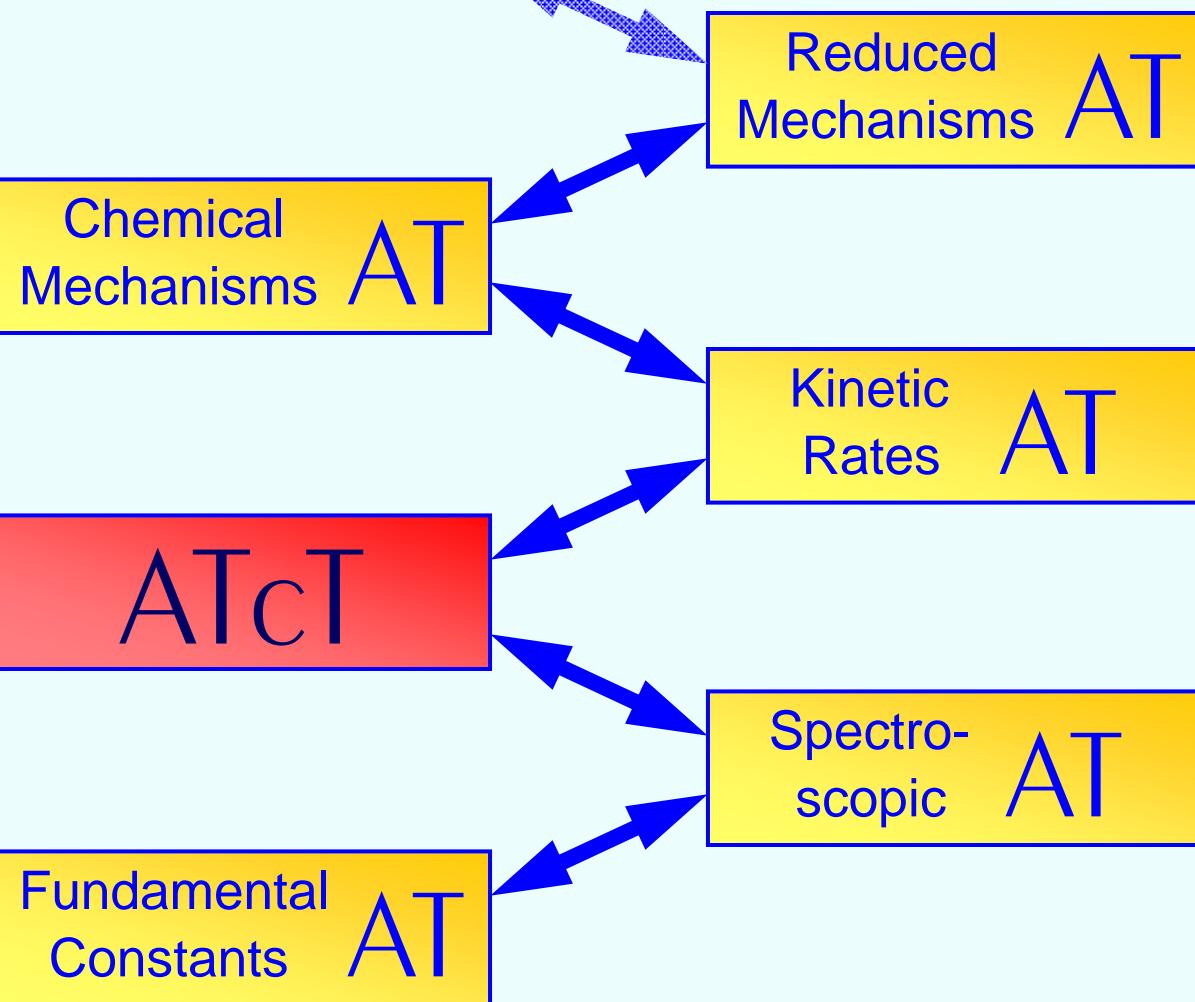
- ATcT are also a **consumer** of information from other scales



ATcT

THE VISION:

STACKED ACTIVE TABLES

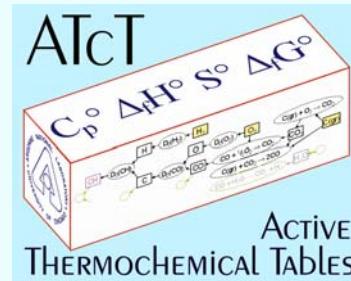


CMCS



visit: <http://cmcs.org>

- go to the Portal
- open an account
- join one of the ATcT groups
- explore beta tester data/software ATcT version



ATcT

Questions, suggestions,
to contribute new data,
or to get latest thermochemistry:
ActiveTables@anl.gov
or rusciic@anl.gov

Thank you for your attention!

The screenshot shows the CMCS homepage with a navigation bar at the top. Below the bar, there's a large banner for "Multi-Scale Chemical Science" featuring various chemical concepts like Quantum Chemistry, Thermo-Chemistry, Kinetics, Mechanisms, and Reaction Chemistry Simulations. A scale bar indicates a range from 10^{-10}m to 10^{-1}m . To the right, a "CMCS Portal" section describes the portal's purpose of enabling collaboration and data sharing between different scientific teams. It includes a "Portal Slide Show" link and a "CMCS News" section with recent updates.

The screenshot shows the ATcT software interface. The top menu bar includes File, Edit, View, Favorites, Tools, Help, and a search bar. The main window has tabs for My Workspace, High Quality Electronic Structure, CMCS Team, Prime Working Groups, and Active Tables. The "Active Tables" tab is selected, showing a search field for "Chemical species" with an example entry of CH4. On the left, a sidebar lists various links: ATcT Home, CMCS Explorer, Announcements, Calendar, Chat, Discussion, Resources, News, Edit Account, and Legend. The bottom of the window shows a "CMCS Explorer Portlet" with an address bar set to "http://cmcs.ca.sandia.gov:9080/the-project/prime".