

THERMODYNAMIC DATA OF IODINE REACTIONS CALCULATED BY QUANTUM CHEMISTRY. TRAINING SET OF MOLECULES

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

This paper focuses on the reactivity of iodine which is the most critical radioactive contaminant with potential short-term radiological consequences to the environment. The radiological risk assessments of ¹³¹I volatile fission products rely on studies of the vapour-phase chemical reactions proceeding in the reactor coolant system (RCS), whose function is transferring the energy from the reactor core to a secondary pressurised water line via the steam generator. Iodine is a fission product of major importance in any reactor accident because numerous volatile iodine species exist under reactor containment conditions. In this work, the comparison of the thermodynamic data obtained from the experimental measurements and theoretical calculations (approaching “chemical accuracy”) is presented. *Ab initio* quantum chemistry methods, combined with a standard statistical-thermodynamical treatment and followed by inclusion of small energetic corrections (approximating full configuration interaction and spin-orbit effects) are used to calculate the spectroscopic and thermodynamic properties of molecules containing atoms H, O and I. The set of molecules and reactions serves as a benchmark for future studies. The results for this training set are compared with reference values coming from an established thermodynamic database. The computed results are promising enough to go on performing *ab initio* calculations in order to predict thermo-kinetic parameters of other reactions involving iodine-containing species.

Keywords: Iodine; Nuclear safety; Gas-phase reactivity; Spectroscopic properties; Thermochemistry; Quantum chemistry.

In the case of severe accident which could occur to a pressurized water reactor (PWR), the potential release of volatile forms of iodine to the environment, molecular iodine or organic iodides, is a particular crucial safety issue

for radiological consequences due to the release of the ^{131}I isotope¹. Iodine, specifically the isotope ^{131}I , is listed among the most critical radio contaminants with potential consequences to people in case of accident-induced iodine releases into the environment².

The primary concerns of radiological risk assessments are volatile fission products, and in particular radio-iodine, whose chemical form is determined by vapour-phase chemical reactions proceeding in the reactor coolant system (RCS) of a PWR. To predict the radiological consequences of an accident, programs were launched³ to simulate all the phenomena involved in a severe accident, such as fuel degradation, release of fission products, transport of aerosols and vapour through the pipes, aerosol behaviour and iodine behaviour in the containment.

One of the main difficulties is that existing validated experimental data on the physicochemical behaviour of iodine up to a fracture in the RCS is inadequate to provide clear-cut, precise answers to the questions² concerning (i) the fraction of iodine present in gaseous or aerosol form at the RCS breaks, i.e. reaching the containment reactor building and (ii) the predominant chemical forms at the break.

Gas-phase chemical reactions through the RCS in the case of severe accidents occur under exceptional conditions: high temperatures and in some cases high pressures. Therefore it is worthwhile to study the system composed of molecules that consist of heavy atoms like iodine or caesium and oxygen/hydrogen close to thermal equilibrium under these conditions. Such studies of molecules require well defined experimental conditions and are difficult to conduct because of the time and cost. The way how to partly alleviate this problem is to calculate the missing thermochemical data for pertinent chemical reaction theoretically. The most common iodine species considered are HI , I_2 and I and their gas-phase hydrated analogues. The purpose of this study is to provide critical test of the performance of the "golden standard" of contemporary quantum chemistry – the coupled cluster theory including single, double and non-iterative triple substitutions (CCSD(T)) – in conjunction with flexible basis set in calculating the spectroscopic and thermochemical properties of molecules included in simple chemical equilibria involving the atoms H , O and I .

Although these molecules have been studied previously and reported extensively in the literature, the pertinent molecular data are not suitable enough for accurate evaluation of the thermochemical quantities since they come from the different levels of the theory (methods and basis sets). Our goal is to attain the benchmark data obtained with the identical method and large basis set for all molecules entering the thermochemistry.

Recently, several papers reporting the experimental and *ab initio* investigations of electronic structure of halogenated molecules and/or their thermochemistry⁴⁻¹² have been published. This interest was primarily motivated by the role of halogen chemistry in the lower atmosphere. In these theoretical studies spectroscopic and thermochemical properties of halogenated diatomics have been studied employing various levels of theory ranging from density functional theory (DFT) using hybrid functionals to CCSD(T). Lazarou et al.⁵ calculated the structural parameters, vibrational frequencies of halogenated molecules using the MP2/6-311G(d) level of theory and bond dissociation energies using the B3P86-DFT method. B3P86 functional shows a systematic tendency to overestimate the binding energy in the open-shell molecules and this trend increases with the size of the system. To refine their results Lazarou et al.⁶ performed coupled cluster study including Douglas–Kroll–Hess scalar relativistic correction^{13,14} and they have used double- and triple-zeta correlation consistent basis sets to estimate the complete basis set limit. The combination of flexible correlation-consistent basis set with CCSD(T) has proven to be cost-effective, leading to thermochemical properties (bond lengths, vibrational frequencies, enthalpies of formation, bond dissociation energies) for a wide range of molecules containing atoms of the first two rows of the Periodic Table. The errors associated with these properties were close to the “chemical accuracy” (± 4 kJ mol⁻¹).

Feller et al.¹² performed thorough analysis of the calculations of thermodynamic quantities for a collection of small halogenated molecules aiming at the chemical accuracy. Their idea of the composite theoretical approach involved extrapolating the results of large basis set, frozen core CCSD(T) calculations to the complete basis set limit (CBS), followed by inclusion of a number of smaller energetic corrections: core-valence correlation, the Douglas–Kroll–Hess scalar relativistic correction, (atomic and molecular) spin-orbit (SO) corrections and higher-order correction that approximates full configuration interaction (FCI). The last one can be estimated using empirical formula proposed by Goodson (Eq. (6) in ref.¹⁵). The combined approach considering all these corrections lead to the mean absolute deviation with respect to experimental enthalpies formation as small as 3.3 kJ mol⁻¹.

The experimental equilibrium distance and harmonic frequency of the HI molecule¹⁶ are 1.609 Å and 2309 cm⁻¹, respectively. Using the MP2 method, Lazarou et al.⁵ obtained for the HI the equilibrium distance $R_e = 1.639$ Å and vibrational frequency $\omega_e = 2289$ cm⁻¹. Feller et al.¹² estimated R_e (1.5998 Å) and ω_e (2354.7 cm⁻¹) in excellent agreement with the experiment. Both values include the corrections to infinite basis, core–valence

correlation, SO coupling and effects of higher excitations by means of the FCI estimate.

The experimental equilibrium distance and harmonic frequency of the I_2 molecule¹⁷ are 2.6663 Å and 214.5 cm⁻¹, respectively. De Jong, Visscher and Nieuwpoort⁴ reported Dirac–Hartree–Fock-coupled cluster (DHF+CCSD(T) with extended basis set) data for I_2 , $R_e = 2.685$ Å and $\omega_e = 217$ cm⁻¹, and concluded that relativistic effects and core–valence correlation need to be included in order to get reliable results. Vala, Kosloff and Harvey⁷ used diatomics-in-molecules method with the spin-orbit correction in conjunction with the relativistic effective core potential and obtained very good agreement ($R_e = 2.672$ Å, $\omega_e = 213$ cm⁻¹) with experimental data. They also observed that their residual SO coupling stabilization at the minimum is 0.095 eV (~9 kJ mol⁻¹). Feller et al.¹² reported slightly worse DK-CCSD(T) results for R_e (2.6473 Å) and ω_e (225.2 cm⁻¹) based on CBS limit, core–valence and FCI contributions.

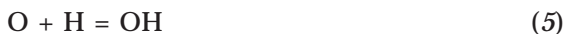
Both these examples prove that the inclusion of both the correction for CBS limit and relativistic effects are *conditiae sine qua non* for the studies aiming at the chemical accuracy. In addition, for the equilibria containing atoms it is equally important to add at least atomic SO correction for heavy atoms.

In this work, we report the spectroscopic and thermodynamic properties of molecules involving atoms H, O and I, which take a part in selected chemical reactions. These molecules constitute a small training set for a critical comparison of their spectroscopic and thermodynamic properties with the experiment. The evaluation of the training set will allow us to set up the computational strategy for the modelling of the PWR iodine chemistry where the experimental data are uncertain, scarce or completely missing. In addition, we want to judge trends along the systematic series of atomic natural orbitals – relativistically contracted (ANO-RCC) sets with increasing contraction length.

METHODS

All *ab initio* calculations have been performed using the MOLCAS program package¹⁸. The following chemical reactions (1)–(7), have been considered





These reactions include both closed-shell and open-shell species. In our computational strategy we have avoided the use of the pseudopotential basis set for iodine and mixed approach in which the geometry is determined at lower level (e.g. DFT). For all molecules, the equilibrium geometries were obtained from potential energy curves calculated using the CCSD(T) method combined with Douglas-Kroll-Hess model to include the scalar relativistic effects. For energy predictions we have chosen the ANO-RCC basis set, suitable for the systems where one expects significant scalar relativistic effects. ANO-RCC is the family of extended relativistic basis sets, constructed to include scalar relativistic effects using the DK Hamiltonian^{13,14,19}. These basis sets were developed by Roos and co-workers^{20,21} for a spectrum of elements from H to Cm and represent an average over several atomic states (both neutral and ionic) and contain functions for correlation of the semi-core electrons. The ANO-RCC primitive sets for H (8s4p3d1f), O (14s9p4d3f2g) and I (22s19p13d5f3g) were contracted to the triple-zeta (TZP, H[3s2p1d]/O[4s3p2d1f]/I[7s6p4d1f]), quadruple-zeta (QZP, H[4s3p2d1f]/O[5s4p3d2f1g]/I[8s7p5d2f1g]) and maximum (LARGE, H[6s4p3d1f]/O[8s7p4d3f2g]/I[10s9p8d5f3g]) contractions to provide sufficiently accurate values of spectroscopic constants. For iodine atom we have adopted three schemes for active electrons in CC calculations. Besides the “standard” freezing of 1s-4p electrons, the variants with 1s-4s and 1s-3d electrons have also been tested with the aim to elucidate the effects of semi-core correlation on spectroscopic properties of I₂ and HI.

The spectroscopic constants (equilibrium distance, rotational constant, harmonic vibrational frequency, anharmonicity correction) were calculated with Dunham sixth degree polynomial fit analysis using reduced coordi-

nate $x = (R - R_e)/R_e$. The bond length for vibrational corrections was optimized with ANO-RCC basis using the CCSD(T) energy curve. The enthalpies, Gibbs energies and entropies for $T = 298.15$ and 600 K were calculated by the standard statistical-thermodynamical treatment²², from equilibrium geometries and molecular energies obtained from *ab initio* calculations. Since we can calculate the CCSD(T) energies around the equilibrium very accurately, we expect that the equilibrium distance R_e and the harmonic vibrational frequency ω_e might be represented slightly better than the anharmonicity $\omega_e x_e$. This difference is usually caused by an increase of CCSD excitation amplitudes for bond stretches larger than about $1.5R_e$ where the anharmonicity of the potential is rather sensitive. It is known²³ that above this distance the inadequacy of single-reference methods (like CCSD used in this work) to describe quasidegeneracy effects is manifested by an increase of single and double excitation amplitudes (t_1 and t_2) from CC expansion. Increase of these quantities above 0.2 (in absolute value) indicates that the single-reference CC approach is inadequate and one has to switch to multi-reference methods. We have used these indicators as a limiting factor for the maximum stretched geometries in calculations of the potential energy curves. For the chemical equilibria included in this study one does not need to go beyond the $1.5R_e$ limit. For this reason, the calculation of the tail of the DK-CCSD(T) potential energy curve was stopped at the interatomic distance when the t_1 or t_2 excitation amplitudes exceeded absolute value 0.15 – 0.20 .

When studying open-shell systems containing heavy atoms, another relativistic effect, spin-orbit (SO) coupling, has to be considered. In our training set, SO correction for iodine atom due to the splitting between the $^2P_{1/2}$ and $^2P_{3/2}$ atomic states can be added, either from the basic atomic spectroscopic database²⁴ or from the calculation²⁵. For iodine atom we have calculated the additional stabilization according to Landé interval rule from the experimental value²⁴. Due to SO coupling our spin-free atomic DK-CCSD(T) energy of iodine atom is lowered by 30.3 kJ mol^{-1} , this contribution was included in reactions (2), (3), (6) and (7). In molecules, the spin-orbit coupling between the ground (closed shell) state and the excited states is almost completely quenched at the equilibrium geometry. This was assumed for HI. Vala, Kosloff and Harvey⁷ have shown that there is residual SO coupling stabilization for I_2 that must be considered. We have used this correction in reactions (1), (2) and (7). The question concerning the SO coupling in I_2 is certainly not trivial. Using simple qualitative explanation, non-polar I_2 will have its iodine components 'more atomic' with certain part of SO resembling that in the iodine atom. Finally, small SO correction based on the

splittings for O and OH taken from the JANAF thermochemical tables²⁶ can be considered for the reaction (5) using Landé interval rule.

RESULTS AND DISCUSSION

Spectroscopic constants of H₂, OH, HI and I₂ molecules are summarized in Table I. In contrast to the popular family of cc-pvXz basis sets the results obtained with three different ANO-RCC contractions used in this paper do not follow equivocal trends typical for the hierarchy of basis sets with the increasing cardinal number X and the use of extrapolation techniques is not straightforward. From our series TZP/QZP/LARGE we can still elucidate the extent of the basis set saturation and judge the quality of the results provided by individual contractions. As a measure of the basis set saturation we have calculated the basis set superposition error (BBSE) for individual components of the equilibria (1)–(7) (Table II). The BSSE for atom A in molecule AB is defined as spurious stabilization: $\delta E_A = E^{AB} - E^A$, where the superscript refers to the basis set. For the evaluation of δE_A , we have used standard counterpoise method introduced by Boys and Bernardi²⁷. DK-CCSD(T) reaction energies are reported in Table III and final total values of the thermodynamic quantities for the training set of the reactions at different levels of approximation are collected in Tables IV–X. Experimental data given in Tables IV–X are taken from²⁸.

The spectroscopic constants (Table I) for the majority of the diatomics show fair agreement with the experiment for the TZP basis. Here (and also for QZP a LARGE contractions) it turned out that R_e alone is rather weak indicator of the quality of the calculational level for light molecules. The performance of the TZP basis set for R_e is significantly worse for HI and I₂ than for light molecules, regardless the frozen-orbitals scheme. There is notable improvement on going to QZP basis set, but the excellent quantitative agreement for R_e was achieved only with the LARGE contraction (deviation from experiment was below 1%). Similar, but more pronounced trends are visible for ω_e .

Harmonic frequency is more sensitive indicator of the quality of the calculation. While the results for H₂ and OH are in excellent agreement with the experiment, molecules HI and I₂ exhibit slightly higher relative deviations, 1–2% for HI and ~5% for I₂. The apparently larger relative deviation for I₂ is caused also by the fact that diatomic iodine is rather weakly bound molecule in the ground state, having the frequency an order of magnitude lower than HI. We have included the anharmonicity constants $\omega_e x_e$ and α_e in Table I just as monitoring quantities for the polynomial fit and to judge

TABLE I
Spectroscopic properties of H₂, OH, HI and I₂ (lengths in Å, frequencies in cm⁻¹)

Frozen orbitals ^a			R _e	ω _e	ω _e x _e	α _e ^b
H ₂		TZP	0.7417	4458.3	165.8	3.615
		QZP	0.7408	4404.3	137.4	3.566
		LARGE	0.7409	4403.1	135.6	3.540
		experiment	0.7414	4401.2	121.3	3.062
OH		TZP	0.9705	3802.4	113.9	0.787
		QZP	0.9699	3765.7	109.4	0.813
		LARGE	0.9697	3765.3	109.4	0.811
		experiment	0.9696	3737.8	84.9	0.724
HI	1s-4p	TZP	1.5883	2425.1	64.4	0.136
		QZP	1.5972	2397.5	61.0	0.133
		LARGE	1.6054	2339.0	46.6	0.104
HI	1s-4s	TZP	1.5837	2425.8	60.3	0.133
		QZP	1.5884	2438.9	53.0	0.126
		LARGE	1.6058	2354.1	46.4	0.103
HI	1s-3d	TZP	1.5821	2432.5	56.1	0.124
		QZP	1.5873	2432.9	45.8	0.101
		LARGE	1.6057	2352.2	34.1	0.073
		experiment	1.6092	2309.0	39.6	0.169
I ₂	1s-4p	TZP	2.7303	212.2	0.66	–
		QZP	2.6628	227.9	0.69	–
		LARGE	2.6632	226.1	0.74	–
I ₂	1s-4s	TZP	2.7222	216.2	0.69	–
		QZP	2.6510	226.0	0.67	–
		LARGE	2.6631	224.6	0.66	–
I ₂	1s-3d	TZP	2.7188	219.2	0.69	–
		QZP	2.6502	227.3	0.64	–
		LARGE	2.6634	224.3	0.72	–
		experiment	2.6660	214.5	0.61	–

^a Frozen orbitals refer to iodine atom. ^b α_e is negligibly small for I₂, see also¹⁶.

how the DK-CCSD(T) approach can reproduce the outer parts of potential energy curves around $1.5R_e$. Although both the first anharmonicity $\omega_e x_e$ and the first-order correction α_e to rotational constant exhibit quite large deviation from experiment, this was expected since our curves still do not cover the whole interval where the anharmonicity effects may become important.

The basis set convergence in the series TZP/QZP/LARGE towards complete basis set is another important issue since for predictive calculations we need very accurate and reliable reaction energies. It can be critically assessed looking at the basis set superposition errors for the atoms in Table II. As expected, the BSSE is negligible for the molecules containing solely hydrogen and oxygen for all three contractions used. The data for iodine indicate that: (i) The TZP and QZP contractions are unacceptable for approaching the chemical accuracy. In addition, the inclusion of deeper semi-core electrons (4p and 4s) increases substantially the BSSE, in accord with Roos et al.²⁰. (ii) The LARGE contraction with stable and relatively small BSSE performs slightly better but it is also far from saturation. For iodine the probable source of the error may lie in the construction of the primitive

TABLE II
Estimates of the basis set superposition error (in kJ mol⁻¹) for the atomic components of the equilibria (1)–(7)

Atom in molecule		Frozen orbitals ^a	TZP	QZP	LARGE
H	(H ₂)		-0.03	-0.02	-0.00
H	(OH)		-0.03	-0.01	-0.00
O	(OH)		-4.43	-1.98	-1.00
H	(HI)		-0.01	-0.01	-0.00
I	(HI)	1s-4p	-27.76	-18.90	-5.05
		1s-4s	-35.24	-32.97	-5.77
		1s-3d	-38.55	-36.52	-5.57
I	(I ₂)	1s-4p	-7.72	-6.48	-2.37
		1s-4s	-11.61	-11.89	-2.73
		1s-3d	-13.63	-13.45	-2.46

^a Frozen orbitals refer to iodine atom.

set, here the expansion stops at g-functions. However we can still accept our reaction energies at the “sub-chemical accuracy” (± 10 kJ mol⁻¹). Due to the approximate nature of the counterpoise correction we treat the energies in Table II as monitoring quantities (the position of the ghost functions is not well defined for the chemical equilibria). They were not included in the final reaction energies but may serve as an information to guess the errors bounds of our thermodynamic quantities.

The reaction energies collected in Table III clearly show that for our training set of reactions one can approach quantitative agreement with experimental data^{26,28} only with the LARGE contraction of ANO-RCC basis set.

TABLE III
CCSD(T) reaction energies (in kJ mol⁻¹) for the series of contractions TZP/QZP/LARGE. Data in parentheses refer to a continued fraction full CI approximation (using Eq. (6) in ref.¹⁵)

Reaction	Frozen orbitals ^a	TZP	QZP	LARGE
H + H ↔ H ₂		-453.4	-456.3	-456.8
H + O ↔ OH		-436.1	-442.3	-442.9 (-444.0)
H ₂ + I ₂ ↔ 2 HI	1s-4p	-77.6	-48.9	-20.6
	1s-4s	-82.8	-64.3	-20.5
	1s-3d	-85.5	-68.4	-20.9 (-16.5)
I + H ₂ ↔ HI + H	1s-4p	110.6	110.1	120.4
	1s-4s	104.3	97.2	120.2
	1s-3d	101.0	93.5	120.3 (123.9)
H + I ₂ ↔ HI + I	1s-4p	-188.2	-159.0	-141.0
	1s-4s	-187.1	-161.4	-140.7
	1s-3d	-186.4	-161.9	-141.1 (-140.4)
I + H ↔ HI	1s-4p	-342.8	-346.2	-336.4
	1s-4s	-349.1	-359.2	-336.6
	1s-3d	-352.4	-362.9	-336.5 (-336.8)
I + I ↔ I ₂	1s-4p	-154.6	-187.2	-195.4
	1s-4s	-162.0	-197.7	-195.9
	1s-3d	-166.0	-201.0	-195.4 (-196.4)

^a Frozen orbitals refer to iodine atom.

The dispersion of TZP and QZP reaction energies is too wide compared with LARGE contraction, this concerns also entries with different number of frozen orbitals for each reaction containing iodine. It follows that the scheme with 1s-3d frozen orbitals in conjunction with the LARGE contraction of the ANO-RCC basis is the most stable one. In the following we will mostly concentrate on the thermodynamic quantities obtained within this computational scheme.

Reaction $H_2 + I_2 \leftrightarrow 2 HI$. Formation of HI is a chemistry textbook example of the reaction between well-behaved closed-shell molecules and it is a linear combination of the next two reactions, where certain cancellation of errors in atomization energies can take place. The high-level *ab initio* methods may be expected to provide data matching the experiment very closely. Indeed, the reaction energies monotonously increase in the row TZP/QZP/LARGE and the agreement with the experiment is very good after inclusion of the correction due to continued fraction approximation to full configuration interaction (0.4 kJ mol⁻¹) and SO correction (-9.2 kJ mol⁻¹). Final

TABLE IV
Thermodynamic quantities for the reaction $H_2 + I_2 \leftrightarrow 2 HI$ ^a

Basic set	T, K	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
TZP	298.15	-85.5	-91.9	21.0
	600	-87.8	-97.4	16.0
QZP	298.15	-68.2	-74.8	22.0
	600	-70.4	-80.6	17.0
LARGE	298.15	-21.6	-28.2	22.0
	600	-23.8	-34.1	17.0
cf approximation	298.15	-21.2	-27.8	
SO corrected		-12.0	-18.6	22.3
experiment		-9.7	-16.2	21.8
cf approximation	600	-23.4	-33.7	
SO corrected		-14.2	-24.5	17.1
experiment		-11.9	-21.8	16.5

^a Based on DK-CCSD(T) energies taken for freezing of 1s-3d electrons.

TABLE V
Thermodynamic quantities for the reaction $\text{H} + \text{I}_2 \leftrightarrow \text{HI} + \text{I}^a$

Basic set	<i>T</i> , K	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
TZP	298.15	-174.6	-176.3	6.0
	600	-176.9	-177.2	0.0
QZP	298.15	-150.1	-152.1	7.0
	600	-152.4	-153.1	1.0
LARGE	298.15	-129.8	-131.8	7.0
	600	-132.1	-132.8	1.0
cf approximation	298.15	-129.1	-131.0	
SO corrected		-150.2	-152.2	6.6
experiment		-147.3	-150.8	11.7
cf approximation	600	-131.4	-133.6	
SO corrected		-152.5	-154.7	3.7
experiment		-149.6	-153.4	6.3

^a Based on DK-CCSD(T) energies taken for freezing of 1s-3d electrons.

TABLE VI
Thermodynamic quantities for the reaction $\text{I} + \text{H}_2 \leftrightarrow \text{HI} + \text{H}^a$

Basic set	<i>T</i> , K	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
TZP	298.15	89.1	84.4	15.0
	600	89.1	79.8	16.0
QZP	298.15	81.9	77.3	16.0
	600	82.0	72.6	16.0
LARGE	298.15	108.2	103.5	16.0
	600	108.3	98.8	16.0
cf approximation	298.15	107.9	103.2	
SO corrected		138.2	133.5	15.7
experiment		137.6	134.6	9.9 ₅
cf approximation	600	108.0	98.5	
SO corrected		138.3	128.8	15.9
experiment		137.7	131.6	10.2

^a Based on DK-CCSD(T) energies taken for freezing of 1s-3d electrons (see Table II).

TABLE VII
Thermodynamic quantities for the reaction $\text{H} + \text{H} \leftrightarrow \text{H}_2$

Basic set	T , K	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS $\text{J mol}^{-1} \text{K}^{-1}$
TZP	298.15	-430.7	-402.9	-93.0
	600	-434.4	-373.3	-102.0
QZP	298.15	-434.0	-406.2	-93.0
	600	-437.7	-376.6	-102.0
LARGE	298.15	-434.4	-406.6	-93.0
	600	-438.1	-377.1	-102.0
experiment	298.15	-436.0	-406.5	-98.9
experiment	600	-439.7	-375.2	-107.5

TABLE VIII
Thermodynamic quantities for the reaction $\text{O} + \text{H} \leftrightarrow \text{OH}$

Basic set	T , K	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS $\text{J mol}^{-1} \text{K}^{-1}$
TZP	298.15	-416.3	-390.8	-86.0
	600	-420.1	-363.5	-94.0
QZP	298.15	-423.2	-397.7	-86.0
	600	-427.0	-370.4	-94.0
LARGE	298.15	-423.8	-398.2	-86.0
	600	-427.5	-370.9	-94.0
cf approximation	298.15	-424.9	-399.4	
SO corrected		-425.3	-399.7	-85.9
experiment		-428.2	-400.7	-92.1
cf approximation	600	-428.6	-372.1	
SO corrected		-429.0	-372.4	-94.3
experiment		-431.6	-371.0	-101.0

enthalpy and Gibbs energy changes are within the ± 4 kJ mol⁻¹ limit and also the agreement between theoretical and experimental entropy change is excellent.

Reaction $H + I_2 \leftrightarrow HI + I$. The reaction energies monotonically increase in the sequence TZP/QZP/LARGE for the process of exothermic iodine abstraction from I_2 . The thermodynamics is influenced by SO coupling in I_2 and I , nevertheless, despite the approximate nature of the respective corrections on both sides of the reaction the agreement with the experiment is still within chemical accuracy. This reaction was studied by Lorenz, Wagner and Zellner²⁹ and their reaction enthalpy (-147 kJ mol⁻¹) matches nicely our calculated value (-150 kJ mol⁻¹) at 298.15 K.

Reaction $I + H_2 \leftrightarrow HI + H$. Proton abstraction from H_2 is the only endothermic process among our set of reactions. Without SO correction there is rather large discrepancy between theory and experiment. The endothermicity is enhanced by inclusion of SO correction for iodine atom bringing the calculated ΔH and ΔG closer to the experimental value. There is a

TABLE IX
Thermodynamic quantities for the reaction $I + H \leftrightarrow HI$ ^a

Basic set	<i>T</i> , K	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
TZP	298.15	-341.6	-318.5	-78.0
	600	-345.3	-293.6	-86.0
QZP	298.15	-352.0	-328.9	-78.0
	600	-355.7	-304.0	-86.0
LARGE	298.15	-326.2	-303.1	-77.0
	600	-329.8	-278.3	-86.0
	298.15	-326.5	-303.4	
	600	-296.2	-273.1	-77.4
		-298.4	-271.9	-88.9
		-330.1	-278.6	
		-299.8	-248.3	-85.9
		-302.0	-243.6	-97.3

^a Based on DK-CCSD(T) energies taken for freezing of 1s-3d electrons.

moderate overestimation of theoretical entropies at both temperatures. This reaction was studied also experimentally by Michael et al.³⁰ and their equilibrium constant for $T = 1901$ K ($pK = 3.458$) based on the ratio of forward and reverse rate constants is in fair agreement with our estimate $pK_{1901K} = 2.085$. Our ΔH agrees very well also with the reaction enthalpy of the reverse reaction $H + HI$, -137 kJ mol⁻¹, reported previously by Lorenz, Wagner and Zellner²⁹.

The first three reactions represent simultaneous decay and formation of pair of bonds, which is manifested by small (positive) entropy change and small-to-medium enthalpy change.

Reactions $H + H \leftrightarrow 2 H$ and $O + H \leftrightarrow OH$. We have included these two addition reactions just for monitoring purposes of the three ANO-RCC contractions used. All three sets (TZP/QZP/LARGE) of thermodynamic data are close to experiment, however, the TZP results clearly indicate that this contraction is not suitable for quantitative purposes, since the errors in both ΔH and ΔG are slightly above chemical accuracy threshold for both temperatures. As we can see, already QZP contraction of ANO-RCC basis is very satisfactory for systems containing only light atoms.

TABLE X
Thermodynamic quantities for the reaction $I + I \leftrightarrow I_2$ ^a

Basic set	T , K	ΔH kJ mol ⁻¹	ΔG kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
TZP	298.15	-167.0	-142.1	-83.0
	600	-168.4	-116.4	-87.0
QZP	298.15	-202.0	-176.9	-84.0
	600	-203.3	-150.9	-87.0
LARGE	298.15	-196.4	-171.3	-84.0
	600	-197.7	-145.4	-87.0
cf approximation	298.15	-197.4	-172.4	
SO corrected		-145.9	-120.9	-84.0
experiment		-151.1	-121.1	-100.7
cf approximation	600	-198.8	-146.5	
SO corrected		-147.3	-95.0	-87.2
experiment		-152.4	-90.2	-103.7

^a Based on DK-CCSD(T) energies taken for freezing of 1s-3d electrons.

Reactions $I + H \leftrightarrow HI$ and $I + I = I_2$. Both reactions are exothermic, the difference in ΔH and ΔG between reaction (6) and (7) reflects the different shape of the potential energy curves for HI and I_2 . The former contains a polarized σ -bond with the Mulliken fractional charges ± 0.4 e on hydrogen and iodine. The potential energy curve for the I_2 molecule has a rather shallow minimum, characterized by low harmonic frequency and consequently small binding energy in comparison with HI or OH. As can be seen from Tables IX and X, our DK-CCSD(T) values for ΔH and ΔG are in very good agreement with the experiment.

CONCLUSIONS

In this paper we have selected small training set of atoms and molecules that are expected to be present in the vapour phase of PWR coolant system. We have demonstrated that high-level *ab initio* correlated method DK-CCSD(T) with sufficiently flexible basis set can provide spectroscopic and thermodynamic data within the limits of chemical accuracy. Following the composite theoretical approach advocated by Feller et al.¹² we have included in final enthalpies and Gibbs energies two types of important corrections: approximate corrections for the remaining correlation energy and SO corrections based on experimental atomic and theoretical molecular data. Using this combined approach we obtained for the training set of reactions the ΔH and ΔG values in very good agreement with literature data. We have shown that the LARGE contraction of the ANO-RCC basis set is suitable for modelling the chemical equilibria containing iodine. Work is in progress with extended set of model reactions of iodine and including also water molecule(s) to simulate the reactivity in the RCS vapour phase of a PWR.

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