Molecular-Level Description of Reaction Equilibrium

CBE 450: Reactor Engineering Fundamentals

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Thermodynamic Properties

Quantum Mechanics can be combined with Statistical Mechanics to provide thermodynamic properties like internal energy, enthalpy, entropy and free energy.

One requires a statistical mechanical model that provides a theoretical framework for expressing thermodynamic properties such as the entropy in terms of molecular level properties, such as the molecular symmetry number, the moment of inertia, the spectrum of normal frequencies, activation barriers to rotation, etc. One must understand that this mapping from QM to SM is in essence a coarse-graining procedure that reduces the number of degrees of freedom in the system. Like any other coarse-graining procedure, the mapping is approximate.

In large part, the most difficult thermodynamic property to determine experimentally or via computation is the entropy. For a polyatomic ideal gas in its ground electronic and nuclear states, the statistical mechanical model splits the entropy into four terms.

$$S_{total} = S_{translational} + S_{rotational} + S_{vibrational} + S_{internal\ rotational}$$

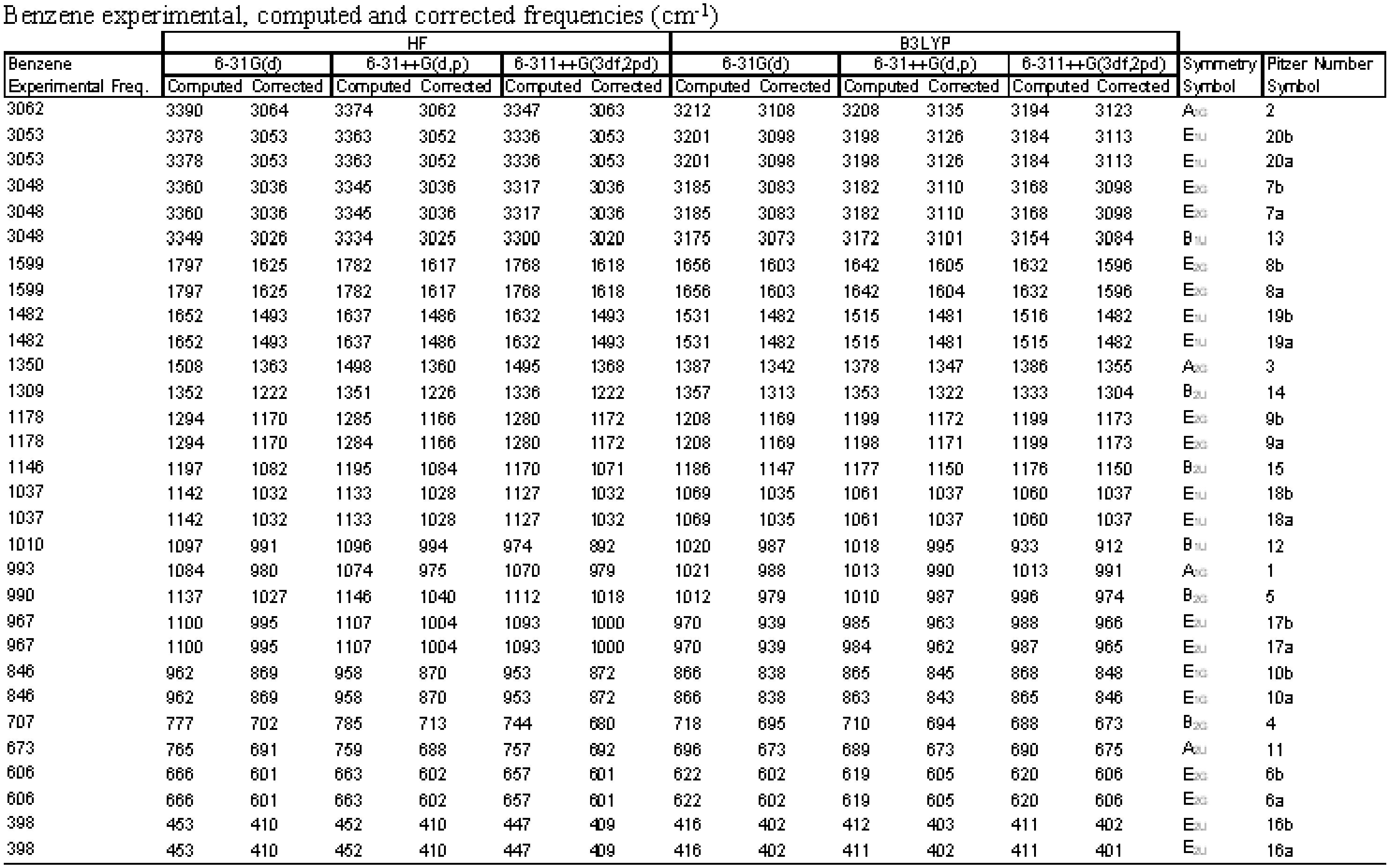
Thermodynamic Properties

The complete set of inputs for a statistical mechanical model used in the determination of these thermodynamic properties is given below. The properties in red come from QM calculations.

- molecular weight (for translation)
- molecular moments of inertia (for rotation)
- symmetry number of molecule (for rotation)
- number of vibrational modes (for vibration)
- spectra of normal frequencies (for vibration)
- number of internal rotors (for internal rotation)
- rotor moments of inertia (for internal rotation)
- rotor activation energies (for internal rotation)
- enthalpy of formation (for energy reference)
- molecular formula (for energy reference)
- reference temperature (for energy reference)

Spectroscopic Properties

Here we show a comparison between experimental and calculated vibrational frequencies of benzene as a function of both method and basis set for benzene.



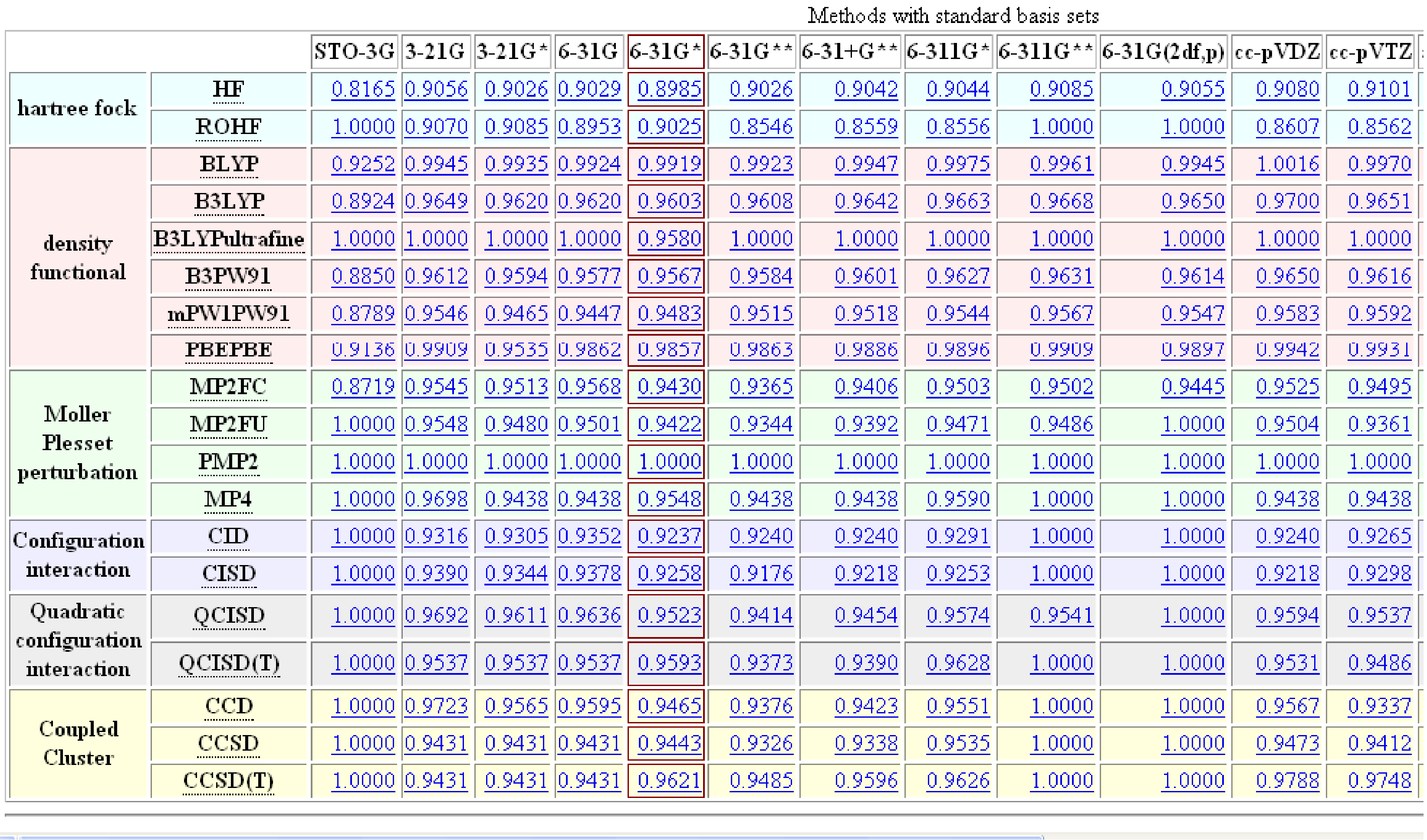
Benzene experimental, computed and corrected frequencies (cm^{-1})

	HF						B3LYP							
Benzene	6-31G(d)		6-31++G(d,p)		6-311++G(3df,2pd)		6-31G(d)		6-31++G(d,p)		6-311++G(3df,2pd)		Symmetry	Pitzer Number
Experimental Freq.	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected	Computed	Corrected	Symbol	Symbol
3062	3390	3064	3374	3062	3347	3063	3212	3108	3208	3135	3194	3123	A_{1g}	2
3053	3378	3053	3363	3052	3336	3053	3201	3098	3198	3126	3184	3113	E_{1u}	20b
3053	3378	3053	3363	3052	3336	3053	3201	3098	3198	3126	3184	3113	E_{1u}	20a
3048	3360	3036	3345	3036	3317	3036	3185	3083	3182	3110	3168	3098	E_{2g}	7b
3048	3360	3036	3345	3036	3317	3036	3185	3083	3182	3110	3168	3098	E_{2g}	7a
3048	3349	3026	3334	3025	3300	3020	3175	3073	3172	3101	3154	3084	B_{1u}	13
1599	1797	1625	1782	1617	1768	1618	1656	1603	1642	1605	1632	1596	E_{2g}	8b
1599	1797	1625	1782	1617	1768	1618	1656	1603	1642	1604	1632	1596	E_{2g}	8a
1482	1652	1493	1637	1486	1632	1493	1531	1482	1515	1481	1516	1482	E_{1u}	19b
1482	1652	1493	1637	1486	1632	1493	1531	1482	1515	1481	1515	1482	E_{1u}	19a
1350	1508	1363	1498	1360	1495	1368	1387	1342	1378	1347	1386	1355	A_{2g}	3
1309	1352	1222	1351	1226	1336	1222	1357	1313	1353	1322	1333	1304	B_{2u}	14
1178	1294	1170	1285	1166	1280	1172	1208	1169	1199	1172	1199	1173	E_{2g}	9b
1178	1294	1170	1284	1166	1280	1172	1208	1169	1198	1171	1199	1173	E_{2g}	9a
1146	1197	1082	1195	1084	1170	1071	1186	1147	1177	1150	1176	1150	B_{2u}	15
1037	1142	1032	1133	1028	1127	1032	1069	1035	1061	1037	1060	1037	E_{1u}	18b
1037	1142	1032	1133	1028	1127	1032	1069	1035	1061	1037	1060	1037	E_{1u}	18a
1010	1097	991	1096	994	974	892	1020	987	1018	995	933	912	B_{1u}	12
993	1084	980	1074	975	1070	979	1021	988	1013	990	1013	991	A_{1g}	1
990	1137	1027	1146	1040	1112	1018	1012	979	1010	987	996	974	B_{2g}	5
967	1100	995	1107	1004	1093	1000	970	939	985	963	988	966	E_{2u}	17b
967	1100	995	1107	1004	1093	1000	970	939	984	962	987	965	E_{2u}	17a
846	962	869	958	870	953	872	866	838	865	845	868	848	E_{1g}	10b
846	962	869	958	870	953	872	866	838	863	843	865	846	E_{1g}	10a
707	777	702	785	713	744	680	718	695	710	694	688	673	B_{2g}	4
673	765	691	759	688	757	692	696	673	689	673	690	675	A_{2u}	11
606	666	601	663	602	657	601	622	602	619	605	620	606	E_{2g}	6b
606	666	601	663	602	657	601	622	602	619	605	620	606	E_{2g}	6a
398	453	410	452	410	447	409	416	402	412	403	411	402	E_{2u}	16b
398	453	410	452	410	447	409	416	402	411	402	411	401	E_{2u}	16a

Kassaee, M.H., Keffer, D.J., Steele, W.V., J. Molecular Structure: THEOCHEM, 800(1-3) 2007 p. 23-34.

Quantum Mechanics Still Requires Experiment

The state of the art of quantum mechanical calculations today is such that one requires an empirical scaling factor to correct vibrational frequencies computed from first principles. Tables of the frequencies have been generated as a function of basis set and method. They are averaged over many compounds.



Methods with standard basis sets

		STO-3G	3-21G	3-21G*	6-31G	6-31G*	6-31G**	6-31+G**	6-311G*	6-311G**	6-31G(2df,p)	cc-pVDZ	cc-pVTZ
hartree fock	HF	0.8165	0.9056	0.9026	0.9029	0.8985	0.9026	0.9042	0.9044	0.9085	0.9055	0.9080	0.9101
	ROHF	1.0000	0.9070	0.9085	0.8953	0.9025	0.8546	0.8559	0.8556	1.0000	1.0000	0.8607	0.8562
density functional	BLYP	0.9252	0.9945	0.9935	0.9924	0.9919	0.9923	0.9947	0.9975	0.9961	0.9945	1.0016	0.9970
	B3LYP	0.8924	0.9649	0.9620	0.9620	0.9603	0.9608	0.9642	0.9663	0.9668	0.9650	0.9700	0.9651
	B3LYPultrafine	1.0000	1.0000	1.0000	1.0000	0.9580	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	B3PW91	0.8850	0.9612	0.9594	0.9577	0.9567	0.9584	0.9601	0.9627	0.9631	0.9614	0.9650	0.9616
	mPW1PW91	0.8789	0.9546	0.9465	0.9447	0.9483	0.9515	0.9518	0.9544	0.9567	0.9547	0.9583	0.9592
	PBEPBE	0.9136	0.9909	0.9535	0.9862	0.9857	0.9863	0.9886	0.9896	0.9909	0.9897	0.9942	0.9931
Moller Plesset perturbation	MP2FC	0.8719	0.9545	0.9513	0.9568	0.9430	0.9365	0.9406	0.9503	0.9502	0.9445	0.9525	0.9495
	MP2FU	1.0000	0.9548	0.9480	0.9501	0.9422	0.9344	0.9392	0.9471	0.9486	1.0000	0.9504	0.9361
	PMP2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	MP4	1.0000	0.9698	0.9438	0.9438	0.9548	0.9438	0.9438	0.9590	1.0000	1.0000	0.9438	0.9438
Configuration interaction	CID	1.0000	0.9316	0.9305	0.9352	0.9237	0.9240	0.9240	0.9291	1.0000	1.0000	0.9240	0.9265
	CISD	1.0000	0.9390	0.9344	0.9378	0.9258	0.9176	0.9218	0.9253	1.0000	1.0000	0.9218	0.9298
Quadratic configuration interaction	QCISD	1.0000	0.9692	0.9611	0.9636	0.9523	0.9414	0.9454	0.9574	0.9541	1.0000	0.9594	0.9537
	QCISD(T)	1.0000	0.9537	0.9537	0.9537	0.9593	0.9373	0.9390	0.9628	1.0000	1.0000	0.9531	0.9486
Coupled Cluster	CCD	1.0000	0.9723	0.9565	0.9595	0.9465	0.9376	0.9423	0.9551	1.0000	1.0000	0.9567	0.9337
	CCSD	1.0000	0.9431	0.9431	0.9431	0.9443	0.9326	0.9338	0.9535	1.0000	1.0000	0.9473	0.9412
	CCSD(T)	1.0000	0.9431	0.9431	0.9431	0.9621	0.9485	0.9596	0.9626	1.0000	1.0000	0.9788	0.9748

Thermodynamic Properties: Benzene

Here we show a comparison between experimental and calculated entropies as a function of both method and basis set for benzene.

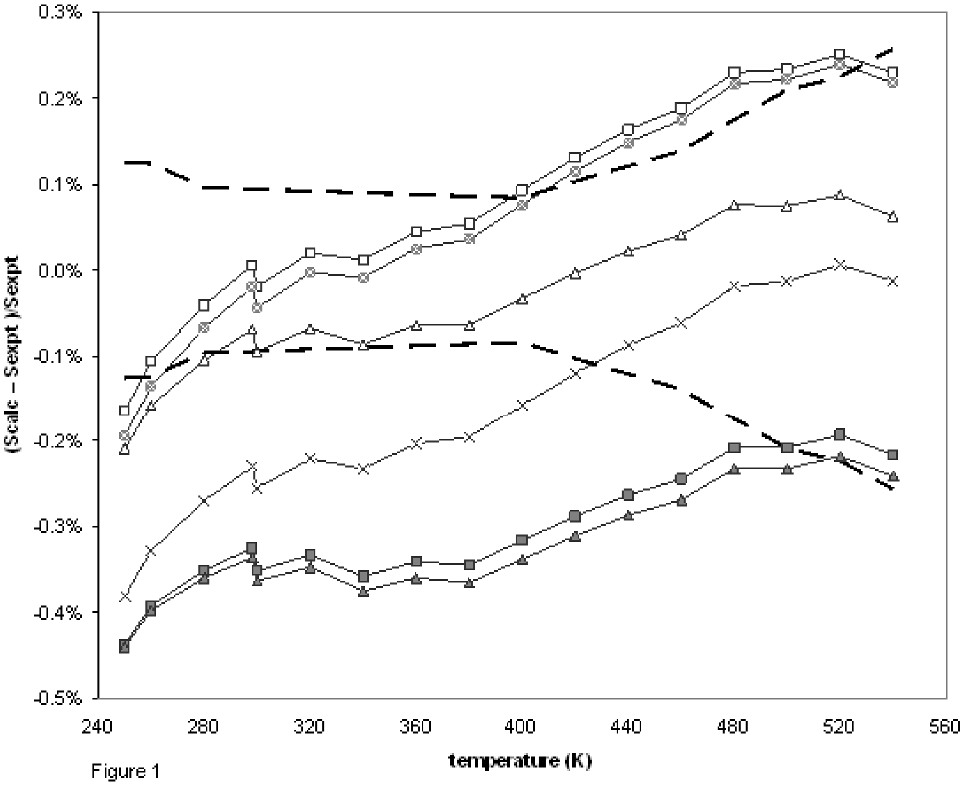
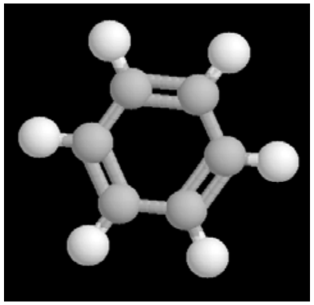


Figure 1



Source: Kassaee, M.H., Keffer, D.J., Steele, W.V., J. Molecular Structure: THEOCHEM, 800(1-3) 2007 p. 23-34.

Equilibrium Distributions

For the ratio of isomers in the ideal gas,

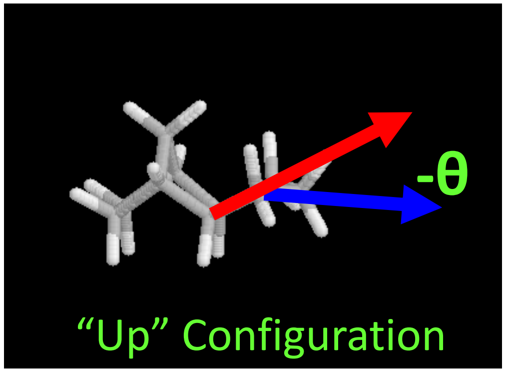
$$\frac{N_1}{N_2} = K_{eq,1-2} = \exp\left(-\frac{\Delta G_{1-2}}{RT}\right)$$

$$= \exp\left(-\frac{\Delta H_{1-2} - T\Delta S_{1-2}}{RT}\right)$$

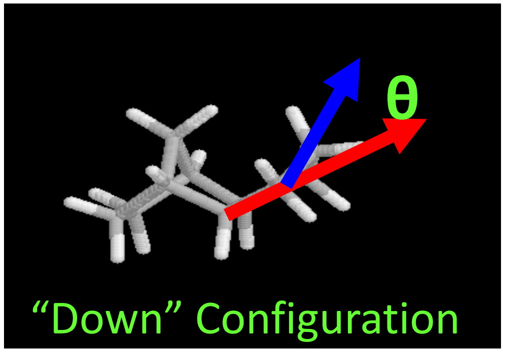
$$= \exp\left(\frac{\Delta S_{1-2}}{R}\right)\exp\left(-\frac{\Delta H_{1-2}}{RT}\right)$$

Thermodynamic Properties: JP-10

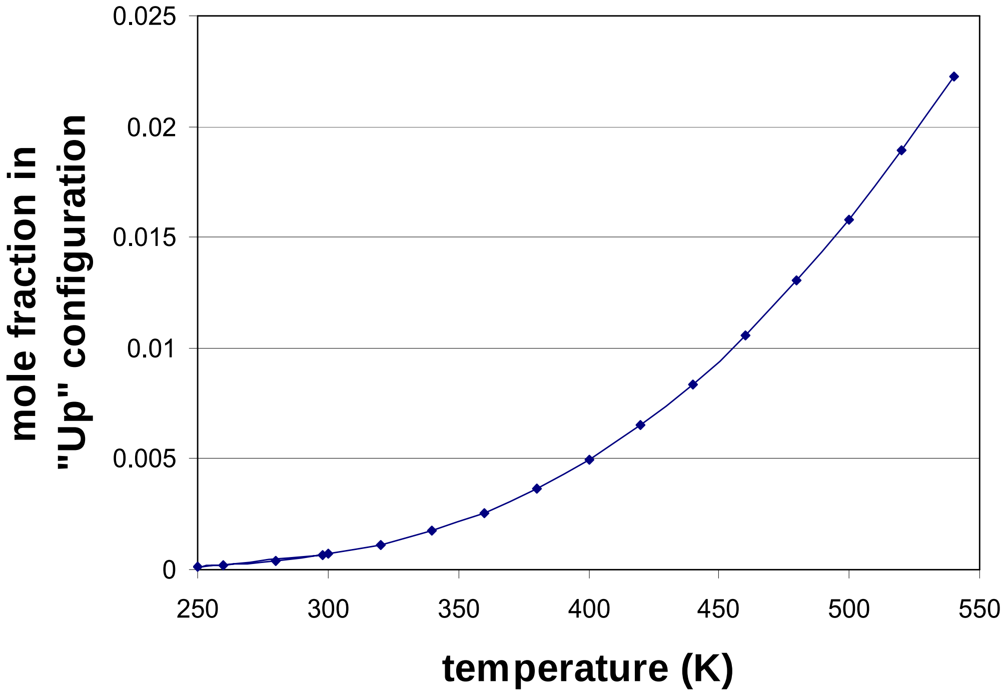
This procedure has been used to compute the relative configuration of the “up” and “down” configurations of the jet fuel, JP-10, as a function of temperature. The Gibbs free energy is calculated at each temperature for each compound. Based on the free energy difference, the relative distribution of configurations is readily determined. In this case, the “down configuration is much more stable and is predominant at low temperatures.



“Up” Configuration



“Down” Configuration



Thermodynamic Properties: dimethylnapthalene

There are 10 dimethylnapthalene isomers. In order to compute the dimethylnapthalene equilibrium distribution, one requires free energies.

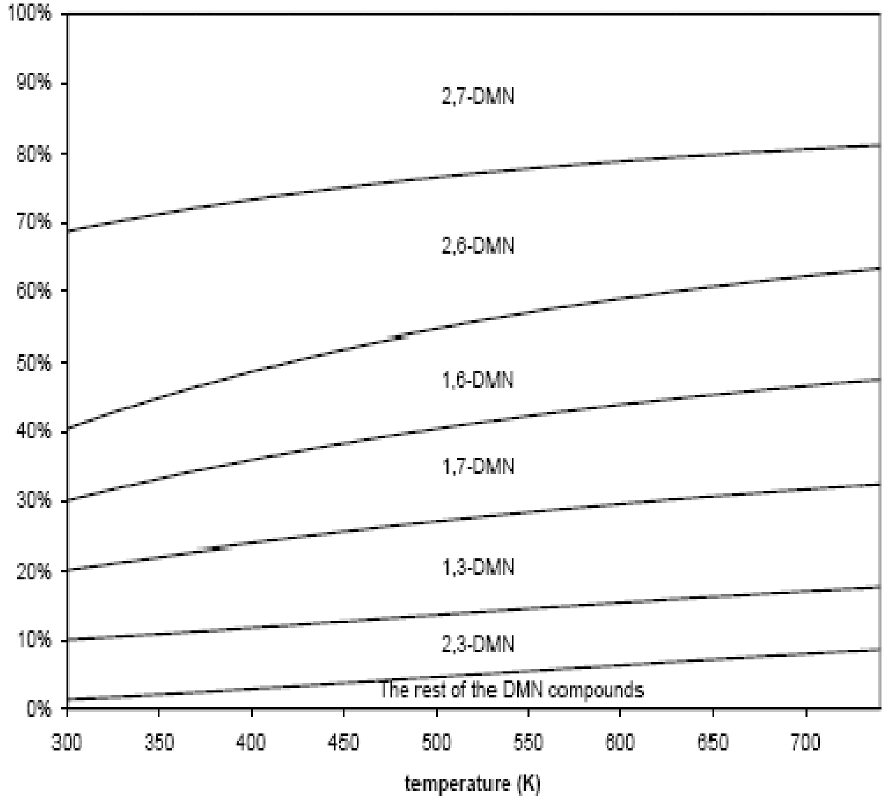
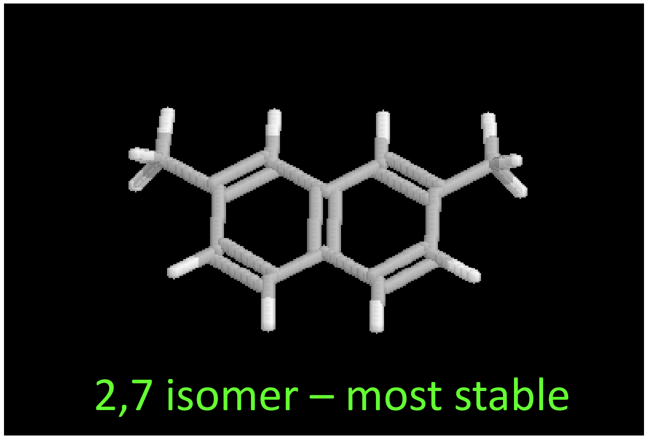
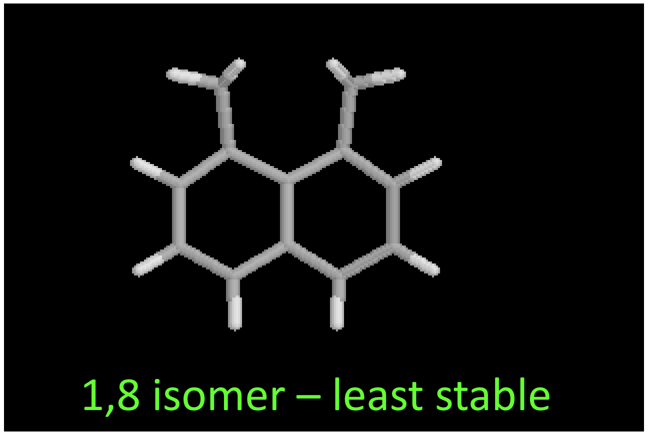


Figure 9 (a): Calculated equilibrium distribution of 2,3-DMN, 1,6-DMN, 1,3-DMN, 1,7-DMN, 2,7-DMN and 2,6-DMN and the sum distribution of the rest of the DMN compounds in the temperature range of 300-740 K with 20 K increments.


2,7 isomer – most stable


1,8 isomer – least stable

Kassaee, M.H., Keffer, D.J., Steele, W.V., *J. Chem. Eng. Data*, **52**(5) 2007 p. 1843-1850.