Focus 3: The Second and Third Laws

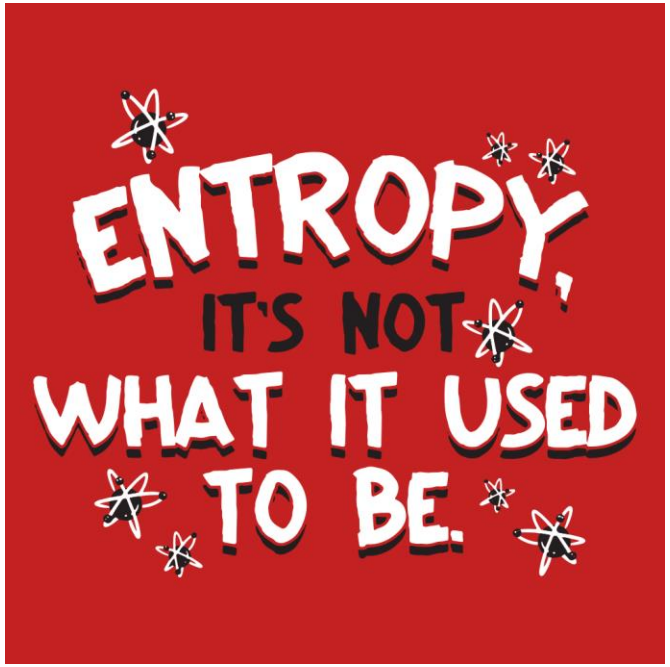
Entropy

Entropy changes in processes

Entropy measurement

Gibbs free energy

Combining 1st and 2nd law



Calorimetric entropy measurement

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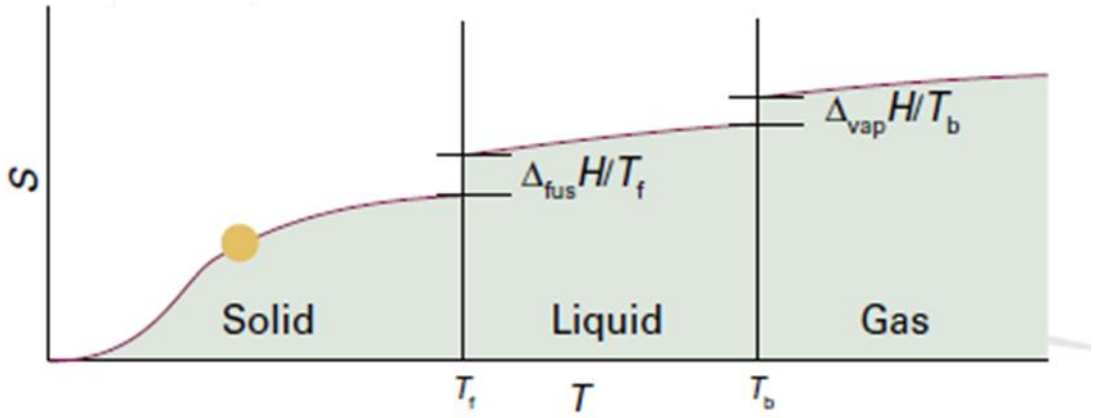
A substance melts at T_f and boils at T_b, then its molar entropy at a particular temperature T above its boiling temperature is



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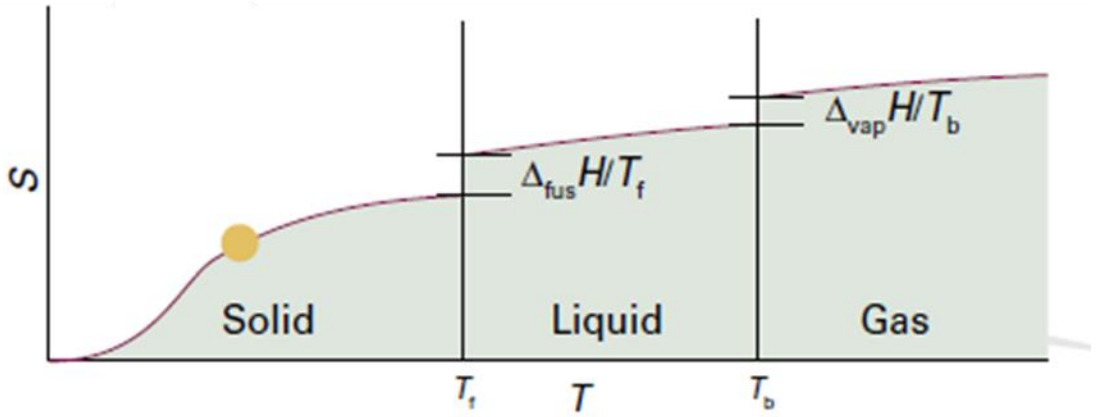

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$$S_m(T) = S_m(0) + \overbrace{\int_0^{T_f} \frac{C_{p,m}(s,T')}{T'} dT'}^{\text{Heat solid to its melting point}} + \overbrace{\frac{\Delta_{fus}H}{T_f}}^{\text{Entropy of fusion}}$$

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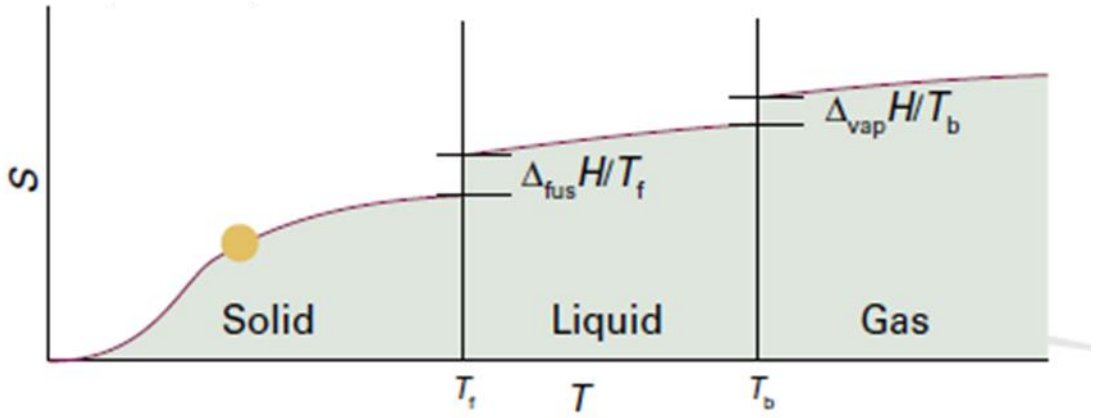

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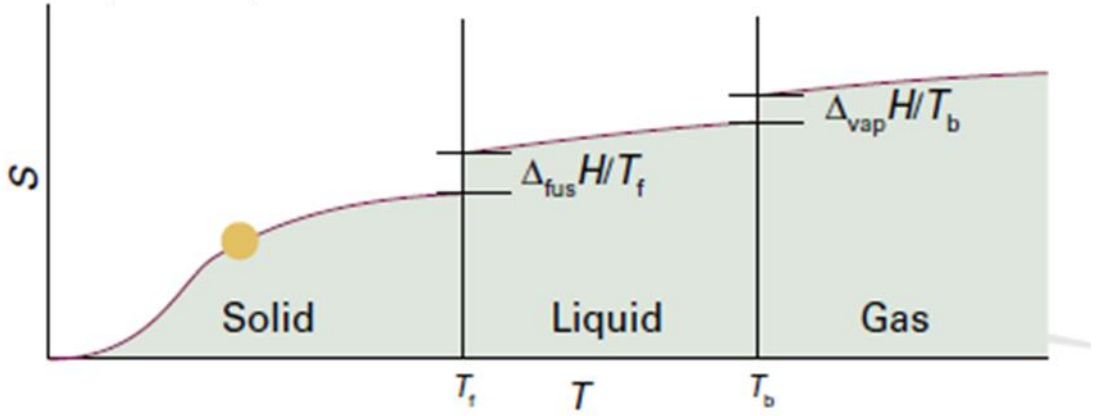

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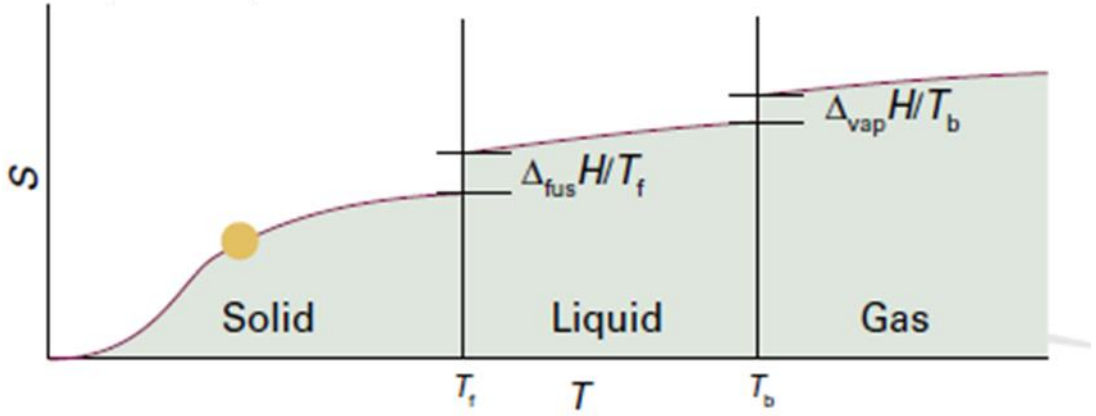

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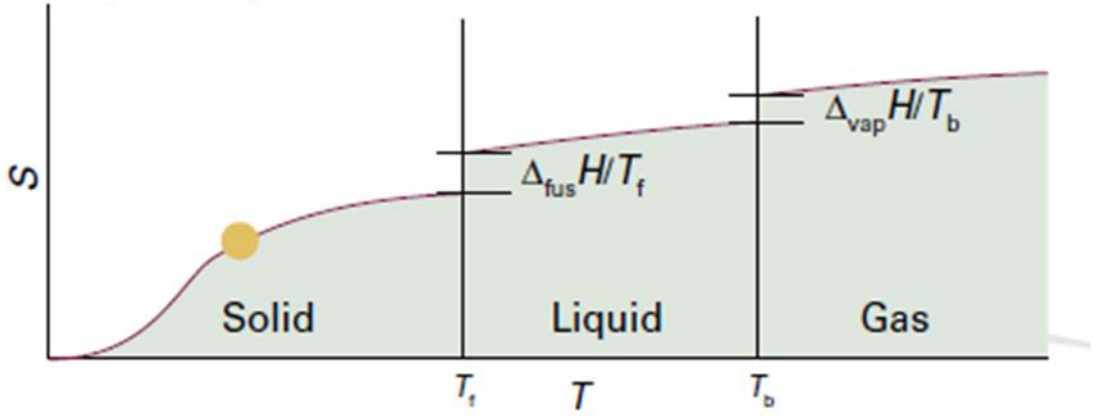
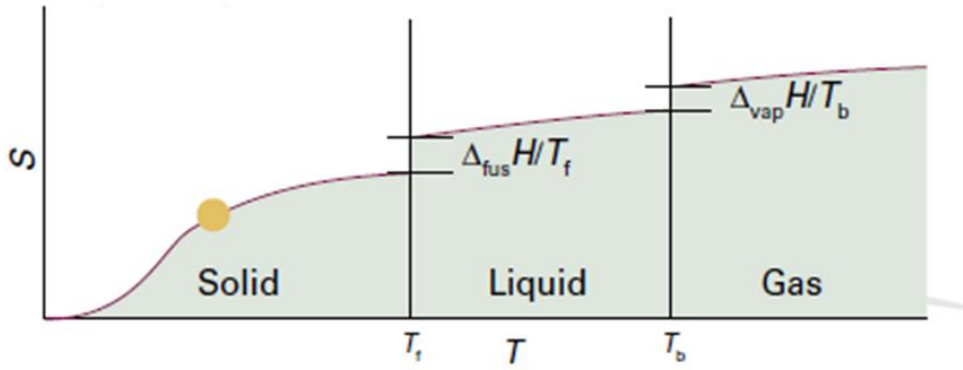
$$+ \overbrace{\int_{T_b}^{T} \frac{C_{p,m}(g,T')}{T'} dT'}^{\text{Heat vapour to the final temperature}}$$



Calorimetric entropy measurement

The standard molar entropy of nitrogen gas at 25 °C

	Contribution to $S_m^{\ominus}/(J\,K^{-1}\,mol^{-1})$
Integration, from 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration, from 35.61 K to 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration, from 63.14 K to 77.32 K	11.41
Vaporization at 77.32 K	72.13
Integration, from 77.32 K to 298.15 K	39.20



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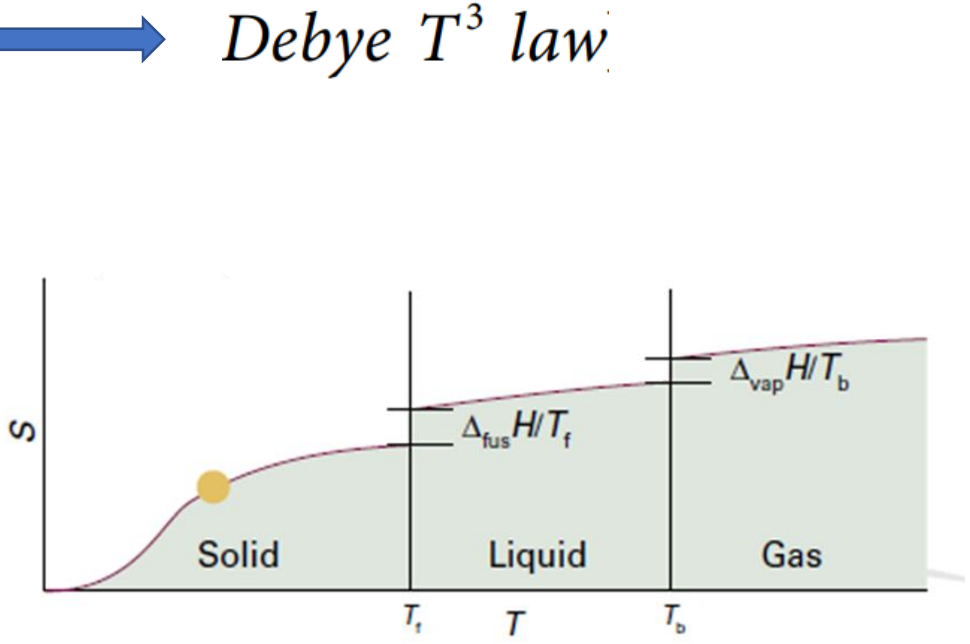

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Assume that the heat capacity of a non-metallic solid is proportional to T^3

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Correction for gas imperfection	0.92
Total	192.06

Debye T^3 law

Assume that the heat capacity of a non-metallic solid is proportional to T^3

Therefore, $S_m^{\ominus}(298.15\,K) = S_m(0) + 192.1\,J\,K^{-1}\,mol^{-1}$

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The molar constant-pressure heat capacity of a certain non-metallic solid at 4.2 K is 0.43 $JK^{-1}mol^{-1}$. What is its molar entropy at that temperature?

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$$S_\mathrm{m}(4.2\,\mathrm{K}) = S_\mathrm{m}(0) + 0.14\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

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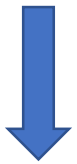

There is only one way of arranging the molecules when they are all in the ground state

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$S = k \ln W$

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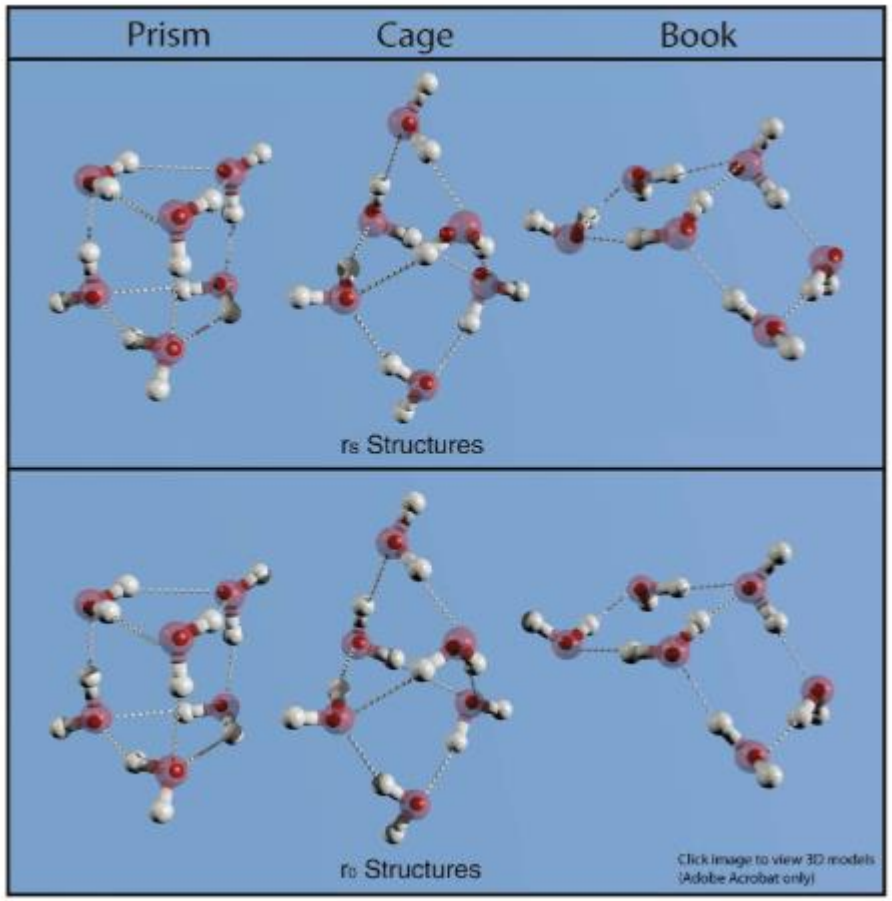
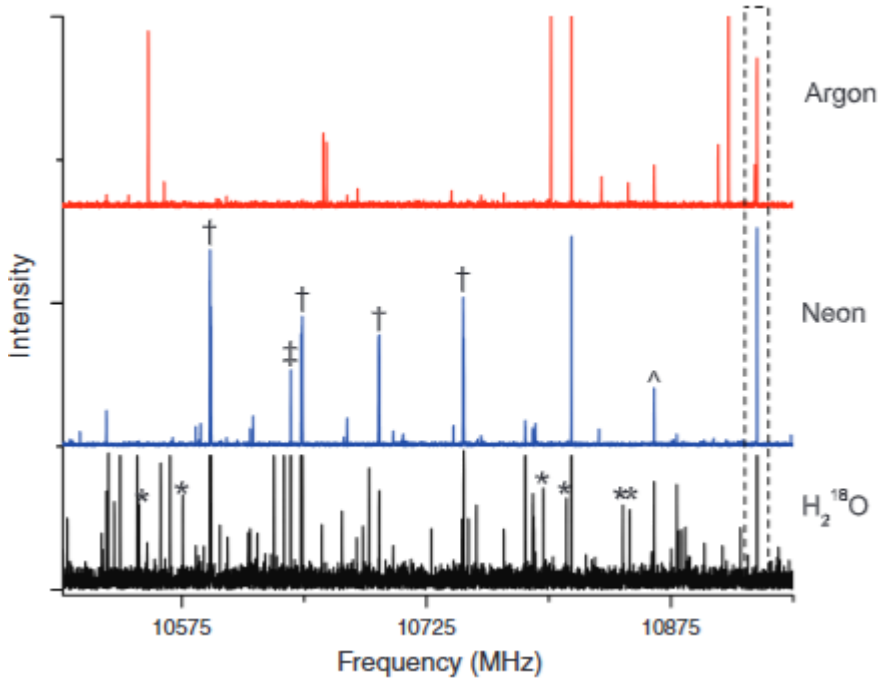
Science
AAAS

Structures of Cage, Prism, and Book Isomers of Water Hexamer from Broadband Rotational Spectroscopy

Cristóbal Pérez *et al.*

Science **336**, 897 (2012);
DOI: 10.1126/science.1220574





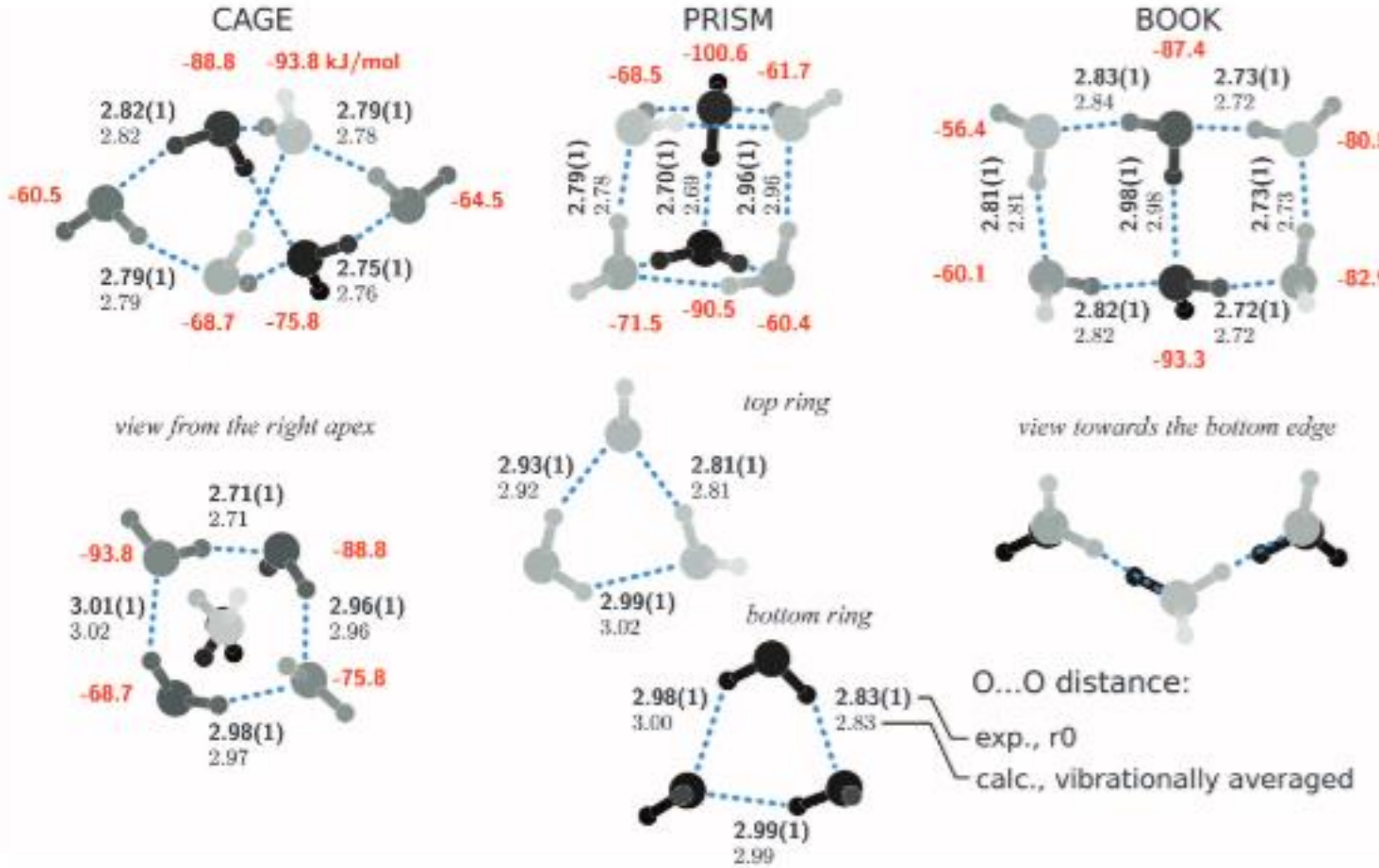


Fig. 4. The experimental r_0-analysis structures are shown for the three water hexamer isomers. The dashed lines indicate the hydrogen-bonding network. The experimental O···O bond distances, in Angstroms, are given in bold with the theoretical values from the vibrationally averaged structures below. The detachment energy for each water molecule in the cluster is given in red.

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Frontiers Article

Broadband Fourier transform rotational spectroscopy for structure determination: The water heptamer

Cristóbal Pérez [a], Simon Lobsiger [a], Nathan A. Seifert [a], Daniel P. Zaleski [a], Berhane Temelso [b], George C. Shields [b,*], Zbigniew Kisiel [c,*], Brooks H. Pate [a,*]

[a] Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22904-4319, USA
[b] Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, PA, 17837, USA
[c] Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

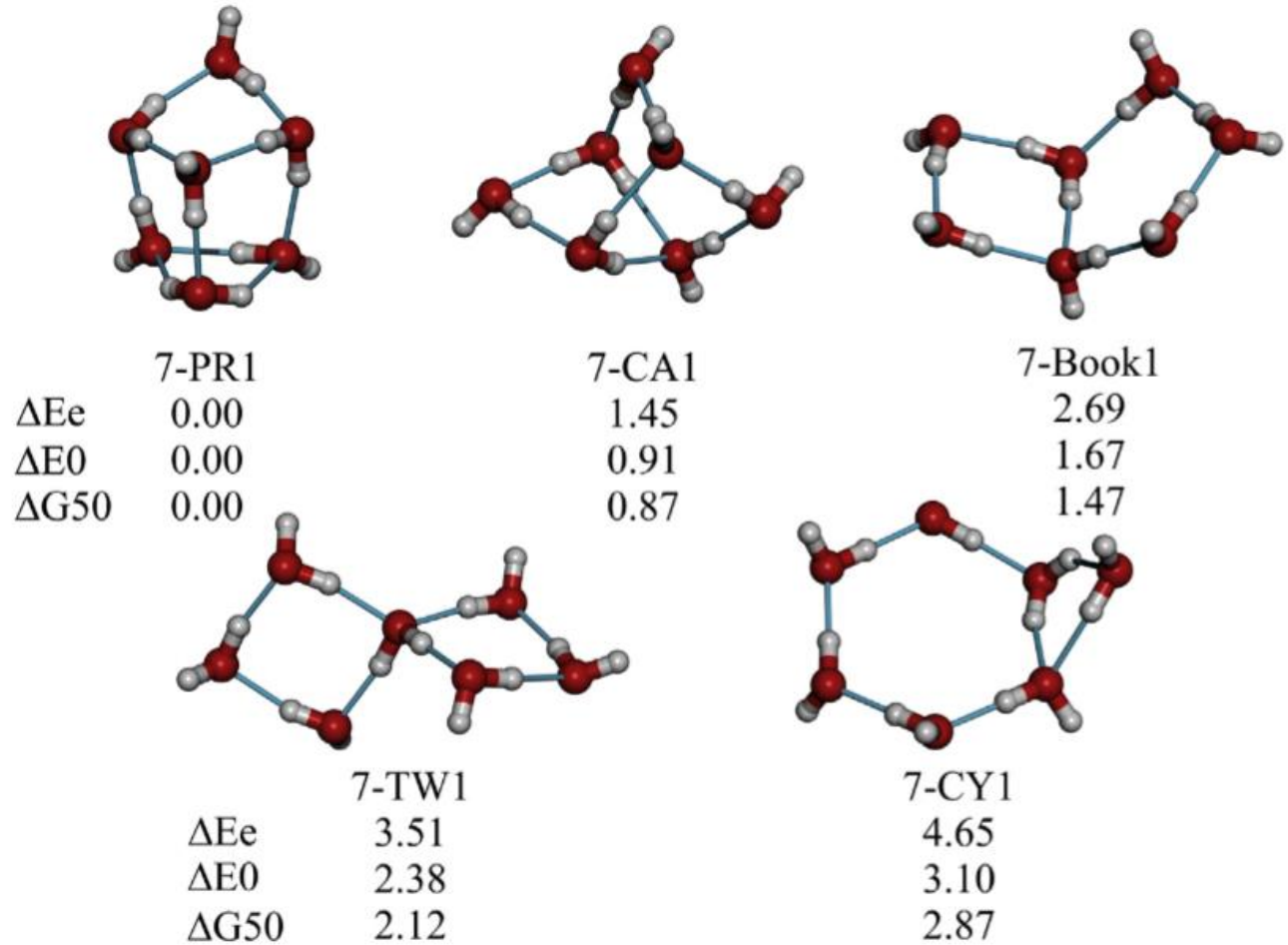

Figure 3. Several low-energy oxygen-atom frameworks of the water heptamer (energy differences in kcal/mol).

Angewandte
International Edition Chemie

DOI: 10.1002/anie.201407447

Water Clusters

Hydrogen Bond Cooperativity and the Three-Dimensional Structures of Water Nonamers and Decamers**

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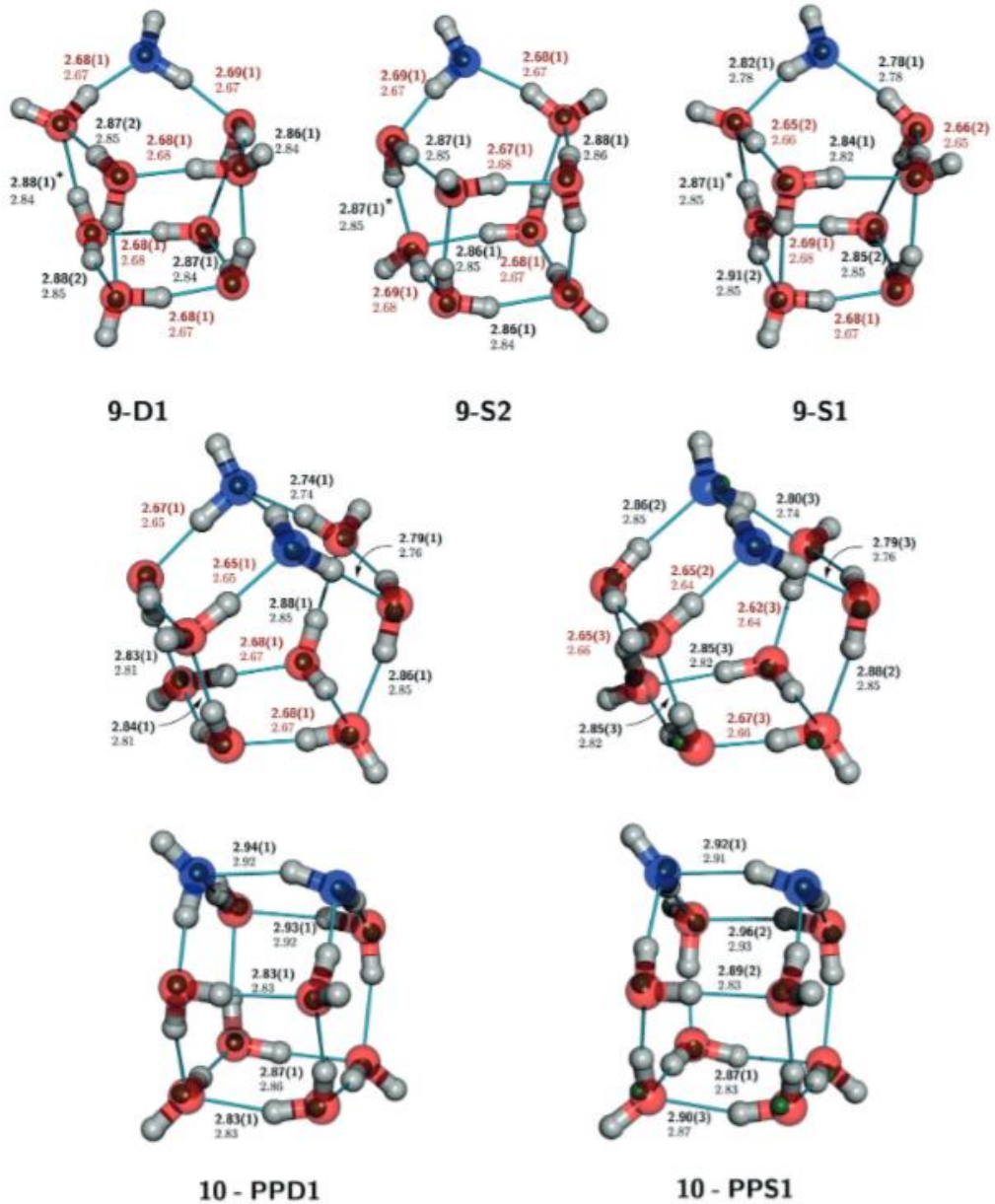

Standard Third Law entropies

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When the substance is in its standard state at the temperature, T

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T}$$

0 J K^{-1} mol^{-1}

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Standard Third-Law entropies at 298 K

	$S_m^{\ominus}/(J\,K^{-1}\,mol^{-1})$
Solids	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.2
Liquids	
Benzene, C_6H_6(l)	173.3
Water, H_2O(l)	69.9
Gases	
Methane, CH_4(g)	186.3
Carbon dioxide, CO_2(g)	213.7
Hydrogen, H_2(g)	130.7
Helium, He(g)	126.2
Ammonia, NH_3(g)	192.4

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$$\Delta_r S^\ominus = S_m^\ominus(H_2O,l) - \{S_m^\ominus(H_2,g) + \tfrac{1}{2} S_m^\ominus(O_2,g)\}$$

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$$= 69.9\,J\,K^{-1}\,mol^{-1} - \{130.7 + \tfrac{1}{2}(205.1)\}\,J\,K^{-1}\,mol^{-1}$$

$$= -163.4\,J\,K^{-1}\,mol^{-1}$$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

The entropy of ions in solution

$$S^{\ominus}(H^{+},aq) = 0$$

Ions in solution [convention]

at all temperatures!

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	$S_m^{\ominus}/(J\ K^{-1}\ mol^{1})^{\dagger}$
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$Mg^{2+}(aq)$	−128
$Cl^-(aq)$	57

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Temperature dependence of reaction entropy

$$\Delta_{\mathrm{r}}C_p^{\ominus}=\sum_{\mathrm{J}}\nu_{\mathrm{J}}C_{p,\mathrm{m}}^{\ominus}(\mathrm{J})$$

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Temperature dependence of reaction entropy

$\Delta_r C_p^{\ominus}$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric numbers that appear in the chemical equation:

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If $\Delta_r C_p^{\ominus}$ is independent of temperature in the range T_1 to T_2 :

$$\Delta_r S^{\ominus}(T_2) = \Delta_r S^{\ominus}(T_1) + \Delta_r C_p^{\ominus} \ln \frac{T_2}{T_1}$$

Calculation

$$\Delta_r S^{\ominus}(T_2) = \Delta_r S^{\ominus}(T_1) + \int_{T_1}^{T_2} \frac{\Delta_r C_p^{\ominus}}{T} \mathrm{d}T$$

The standard reaction entropy for $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ at 298 K is $-44.42\,J\,K^{-1}\,mol^{-1}$, and the molar heat capacities at constant pressure of the molecules are $H_2O(g)$: $33.58\,J\,K^{-1}\,mol^{-1}$; $H_2(g)$: $28.84\,J\,K^{-1}\,mol^{-1}$; $O_2(g)$: $29.37\,J\,K^{-1}\,mol^{-1}$.

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$$\Delta_r C_p^{\ominus} = C_{p,m}^{\ominus}(H_2O,g) - C_{p,m}^{\ominus}(H_2,g) - \tfrac{1}{2} C_{p,m}^{\ominus}(O_2,g)$$

$$= -9.94\,J\,K^{-1}\,mol^{-1}$$

Calculation

$$\Delta_r S^{\ominus}(T_2) = \Delta_r S^{\ominus}(T_1) + \Delta_r C_p^{\ominus} \ln \frac{T_2}{T_1}$$

The standard reaction entropy for $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ at 298 K is $-44.42\,J\,K^{-1}\,mol^{-1}$, and the molar heat capacities at constant pressure of the molecules are $H_2O(g)$: $33.58\,J\,K^{-1}\,mol^{-1}$; $H_2(g)$: $28.84\,J\,K^{-1}\,mol^{-1}$; $O_2(g)$: $29.37\,J\,K^{-1}\,mol^{-1}$.

$$\Delta_r C_p^{\ominus} = C_{p,m}^{\ominus}(H_2O,g) - C_{p,m}^{\ominus}(H_2,g) - \tfrac{1}{2} C_{p,m}^{\ominus}(O_2,g)$$

$$= -9.94\,J\,K^{-1}\,mol^{-1}$$

$$\Delta_r S^{\ominus}(373\,K) = -44.42\,J\,K^{-1}\,mol^{-1} + (-9.94\,J\,K^{-1}\,mol^{-1}) \times \ln \frac{373\,K}{298\,K}$$

$$= -46.65\,J\,K^{-1}\,mol^{-1}$$

Focus 3: The Second and Third Laws

Entropy

Entropy changes in processes

Entropy measurement

Free energy

Combining 1st and 2nd laws