Chem 391 in a Nutshell

Goals for the semester:

1. Tools to **measure** structure (spectroscopy)
   How they work (a little) and what they measure (a lot)

2. Organizing principles to **describe** structure
   Just like words for different colors can help organize visual world

3. Tools to **measure** function
   Equilibrium can be measured by K, reaction rates measured by k

4. Organizing principles to link function to structure: **thermodynamics**
   Think consistently about contributions of ΔH and ΔS to spontaneity (ΔG).

Powers of 10

K	ΔG° (kcal/mol)	ΔG° (kJ/mol)
10^{-10}	+14	+57
0.001	+4.2	+17.1
0.01	+2.8	+11.4
0.1	+1.4	+5.7
1	0	0
10	-1.4	-5.7
100	-2.8	-11.4
1000	-4.2	-17.1
10^{10}	-14	-57

Covalent Bonding

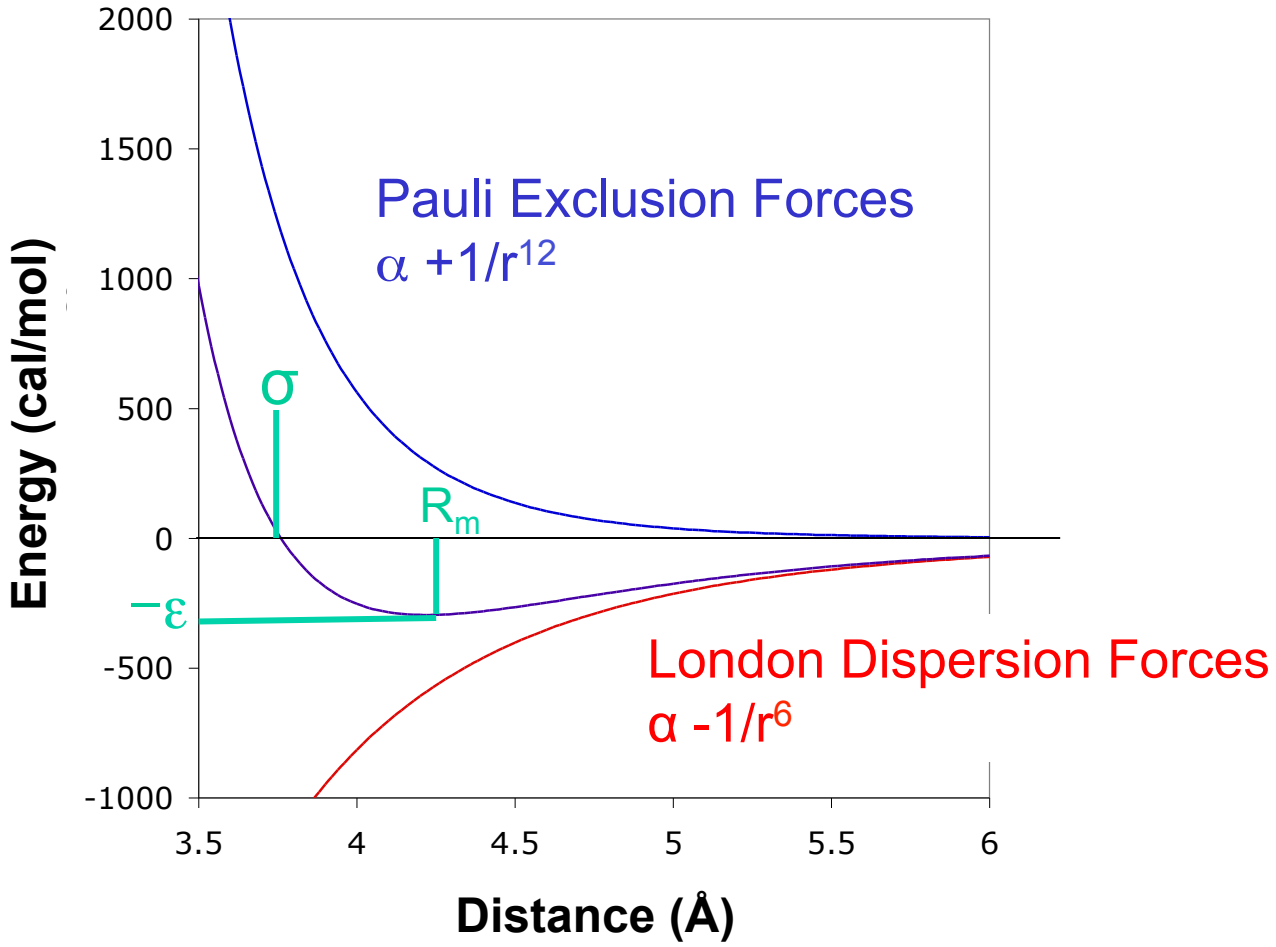
C-C	83 kcal/mol	1.54 Å
C=C	147 kcal/mol	1.34 Å
C-O	86 kcal/mol	1.43 Å
C=O	127 kcal/mol	1.20 Å
C-H	99 kcal/mol	1.09 Å
O-H	111 kcal/mol	0.96 Å
N≡N	227 kcal/mol	1.10 Å

Some Intermolecular Interactions

	ΔH ($^{kcal}/_{mol}$)	**dist. (Å)**
$CH_4 \bullet CH_4$	0.3	3.5
$SiH_4 \bullet SiH_4$	0.6	4.2
$H_2O \bullet CH_4$	0.9	3.5
HF•HF	2.9	2.7
HCl•HCl	1.2	3.8

Lennard-Jones Potential

$$E = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



van der Waals Interactions

Atom	α Polarizability ($Å^3$)	vdW Radius (Å)	vdW Contact Distance (Å)	Min. Contact Energy ($^{kcal}/_{mol}$)
H	0.7	1.20	1.50	0.02
O	0.8	1.40	1.60	0.21 (hydroxyl)
N	1.1	1.55	1.70	0.17 (amide)
C	1.8	1.70	1.80	0.11 (sp^3)
S	2.9	1.80	2.00	0.25 (thioether)

Hydrogen Bonding

(distance measured between heavy atoms)

Bond	Mean Distance (Å)	Range (Å)
N-H···N	3.10	2.88-3.38
N-H···O		
Amide NH	2.93	2.55-3.04
Amino NH	3.04	2.57-3.22
O-H···N	2.80	2.62-2.93
O-H···O		
Alcohol OH	2.74	2.55-2.96
Water OH	2.80	2.65-2.93

H-bonding in Water

TABLE I

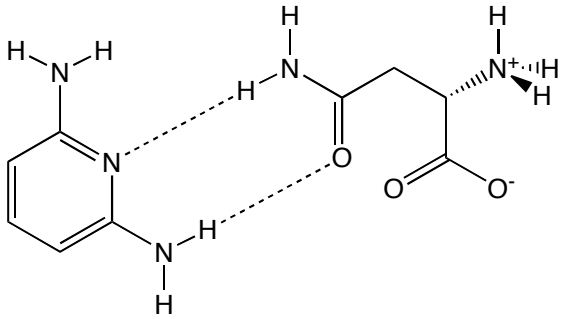
THERMODYNAMICS OF INTERAMIDE HYDROGEN BOND FORMATION BY N-METHYLACETAMIDE AT 25°

Solvent	Association constant for dimerization, k_2	$\Delta F°$, kcal. mole^{-1}	$\Delta H°$, kcal. mole^{-1}	$\Delta S°$, gibbs mole^{-1}
Carbon tetrachloride	4.7 (5.8)	−0.92	−4.2	−11
Dioxane	0.52 (0.58)	0.39	−0.8	− 4
Water	0.005 (0.005)	3.1	0.0	−10

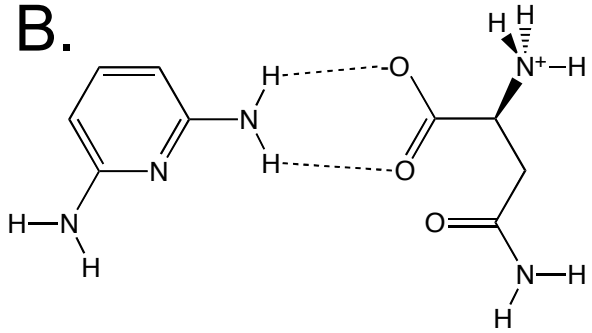
Klotz & Franten (1962) *JACS* **84**, 3461-3466

Which of these H-bonding Schemes is Satisfactory?

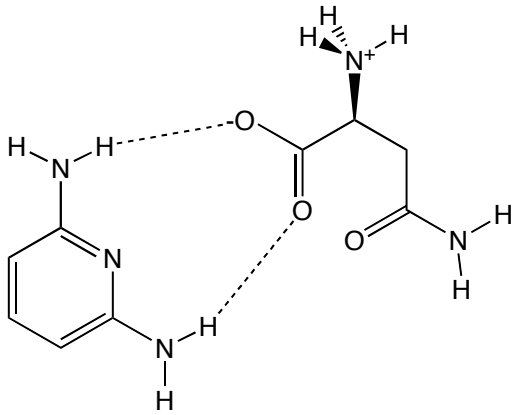
A.



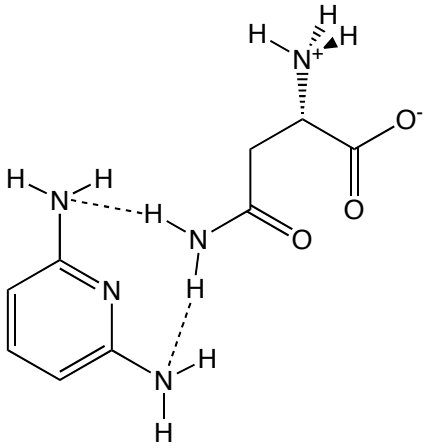
B.



C.



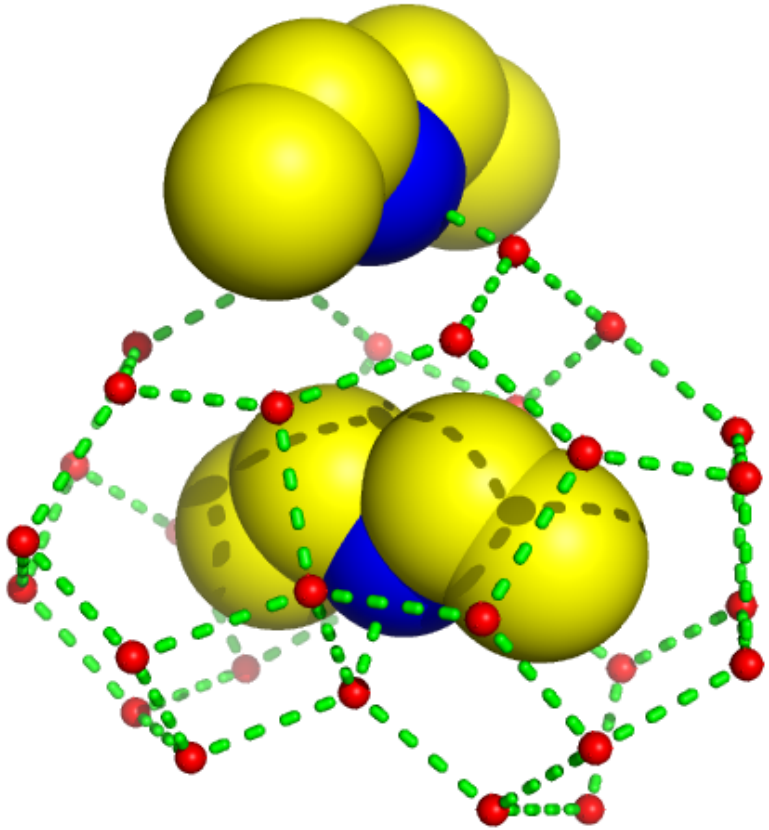
D.



Thermodynamics of methane dissolving in H_2O and CCl_4

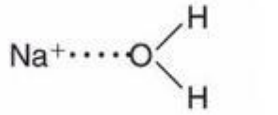
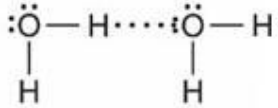
Transfer	**ΔG°** ($^{kcal}/_{mol}$)	**ΔH°** ($^{kcal}/_{mol}$)	**ΔS°** ($^{cal}/_{mol \cdot K}$)
$CH_{4(g)} \rightarrow CH_{4(H2O)}$	+6.3	-3.2	-32
$CH_{4(g)} \rightarrow CH_{4(CCl4)}$	+3.5	-0.5	-14
$CH_{4(CCl4)} \rightarrow CH_{4(H2O)}$	+2.8	-2.7	-18

Diethylamine Hydrate (Clathrate)



Jordan & Mak (1967) *J Chem Phys* **47**, 1222

Electrostatic Forces

Nonbonding (Intermolecular)			E (kJ/mol)	
Ion-dipole		Ion charge–dipole charge	40–600	
H bond		Polar bond to H– dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	
Ion–induced dipole		Ion charge–polarizable e⁻ cloud	3–15	
Dipole–induced dipole		Dipole charge–polarizable e⁻ cloud	2–10	
Dispersion (London)		Polarizable e⁻ clouds	0.05–40	

http://itl.chem.ufl.edu/2045/lectures/lec_g.html