Binding (or Cohesive) Energy

Definition and Constraints

The binding or cohesive energy $\epsilon_c$of a substance (either liquid or solid) is the energy required to break all the bonds associated with one of its constituent molecules. It is, therefore a measure of the *inter*-molecular energy for a substance. We spend time considering these numbers because they form the basis for many OOM estimates, from density to sound speed to heat capacity.

We know that *intra*-molecular bonds that hold atoms together in a molecule (e.g. the O-H bond in water) are generally much stronger than inter-molecular bonds. After all, when you heat water, it boils to form water vapor, but the water molecules do not decompose into, say, O_2 and H_2. This means that the thermal energy of H_2O even at high temperature is not enough to break the intra-molecular bonds, thus implying that these intra-molecular bonds are stronger than those holding the substance together.

Here's a table of typical energies for such bonds:

Bond	Bond energy (eV)
C-C	6.3
H-H	4.5
O-H	4.4
Na-Cl	4.3
Fe-O	4.0

Thus, whatever we estimate to be the cohesive bond strengths for liquids and solids, the values should be smaller than these!

Liquids

This represents the energy required to separate a molecule from the liquid phase and transfer it to the vapor phase. This represents almost entirely the inter-molecular binding energy of the liquid molecules, since this energy in gases is extremely small (and in fact zero for ideal gases).

Liquid	ΔH_{vap}(kJ/mol)	ϵ_c(eV per molecule)
Water	41	0.4
Ammonia	23	0.2
Butane	21	0.2
Ethanol	39	0.4
Methane	8.2	0.08
Propane	16	0.2

From these values, we can estimate the binding energies as shown in the Table, which is simply converting from units of kJ/mol to eV per molecule. Note that this conversion is almost exactly 10^{-5}(eV per molecule) / (kJ/mol).

We conclude, then, that the binding energies in liquids range from 0.1 to 0.4 eV, depending on the polarity of the molecules. Molecules that have greater permanent dipoles (i.e. one end strongly positive, one end strongly negative, as in water where the oxygen is strongly negative and the hydrogens positive). If you know nothing about the liquid, 0.2 eV is a reasonable rule of thumb that gets you within a factor of 2. Note that these values are much smaller than the intra-molecular bond energies, so we've satisfied that constraint. Note that in order to properly compare these values, one should determine how many neighbors a typical liquid molecule has, and divide the cohesive energies in the table above by that number of neighbors to estimate the energy of a single molecule-molecule interaction.

Solids

For solids, we can play the same game, although one disadvantage of this method is that for many solids of interest (like rocks), heats of vaporization are not readily available. Below are some values for elements.

If you focus only on the solid elements, you can see that values range from 100 (sodium) to 800 (tungsten) kJ/mol, with typical values in the range of 300 to 400 kJ/mol for the most common elements like Al, C, Si, Fe, Ni and Cu. This gives metal binding energies that are about an order of magnitude larger than that for liquids, i.e. $\epsilon_c \sim$3 to 4 eV. (Note that for a typical molecule in a solid with 6 neighbors, this yields values of $\sim$0.5 eV per bond, which again is smaller than the intra-molecular bond energies and therefore strikes us as reasonable.) In reality, these numbers are a bit high, perhaps because vaporization of many solids occurs at temperatures of order 10^3 K, which is far enough from room temperature as to make these heats

of vaporization not directly relevant to room temperature cohesive energies without some correction. Sanjoy's estimates of $\epsilon_c \sim 1$ to 2 eV for a typical cohesive energy is probably a bit better, so we can use these as representative values for solids.

Enthalpies of vaporization of the elements in kJ/mol

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 0.44936																	He 0.0845
2	Li 145.92	Be 292.40											B 489.7	C 355.8	N 2.7928	O 3.4099	F 3.2698	Ne 1.7326
3	Na 96.96	Mg 127.4											Al 293.4	Si 384.22	P 12.129	S 1.7175	Cl 10.2	Ar 6.447
4	K 79.87	Ca 153.6	Sc 314.2	Ti 421	V 452	Cr 344.3	Mn 226	Fe 349.6	Co 376.5	Ni 370.4	Cu 300.3	Zn 115.3	Ga 258.7	Ge 330.9	As 34.76	Se 26.3	Br 15.438	Kr 9.029
5	Rb 72.216	Sr 144	Y 363	Zr 581.6	Nb 696.6	Mo 598	Tc 660	Ru 595	Rh 493	Pd 357	Ag 250.58	Cd 100	In 231.5	Sn 295.8	Sb 77.14	Te 52.55	I 20.752	Xe 12.636
6	Cs 67.74	Ba 142	*	Hf 575	Ta 743	W 824	Re 715	Os 627.6	Ir 604	Pt 510	Au 334.4	Hg 59.229	Tl 164.1	Pb 177.7	Bi 104.8	Po 60.1	At 114	Rn 16.4
7	Fr *n/a*	Ra 37	**	Rf *n/a*	Db *n/a*	Sg *n/a*	Bh *n/a*	Hs *n/a*	Mt *n/a*	Ds *n/a*	Rg *n/a*	Uub *n/a*	Uut *n/a*	Uuq *n/a*	Uup *n/a*	Uuh *n/a*	Uus *n/a*	Uuo *n/a*
* **Lanthanides**				La 414	Ce 414	Pr *n/a*	Nd *n/a*	Pm *n/a*	Sm *n/a*	Eu *n/a*	Gd *n/a*	Tb *n/a*	Dy *n/a*	Ho *n/a*	Er *n/a*	Tm *n/a*	Yb *n/a*	Lu *n/a*
** **Actinides**				Ac *n/a*	Th 514.4	Pa *n/a*	U *n/a*	Np *n/a*	Pu *n/a*	Am *n/a*	Cm *n/a*	Bk *n/a*	Cf *n/a*	Es *n/a*	Fm *n/a*	Md *n/a*	No *n/a*	Lr *n/a*

Figure 1: