

Section 7 – Questions from Shriver and Atkins

2.8 N_2 has three bonds, one σ and two π (or “ N_4 ” = 2 N_2 , with six total bonds, two σ and 4 π). P_4 has six σ bonds. In both cases the σ bonds are stronger than the π bonds, but in the case of N_2 , the π -bonds are not that much weaker, and so the entropy term (which favours 2 N_2 instead of N_4) overcomes the small difference in energy between the σ and π bond strengths. In the case of P_2 , where the π bond is much weaker, the entropy term cannot overcome the difference, so P_4 is formed instead. Put another way, the π -bonds are strong enough in N_2 to make 2 N_2 feasible, while in P_2 the π bonds are not strong enough.

4.23 Remember the organic method – the strongest acid has the most stable conjugate base. By this definition, HS^- is less stable than HSe^- because the latter has a bigger atom and is better able to sustain a negative charge. Thus, HSe^- is the more stable conjugate base and H_2Se is the stronger acid.

4.26 (a) Row 1: This is the exception series – BF_3 should be the strongest because F is the most electronegative halogen, but it also allows π -donation into the empty B p_z orbital, thus negating much of the acid strength. Therefore, BBr_3 is the strongest Lewis acid.

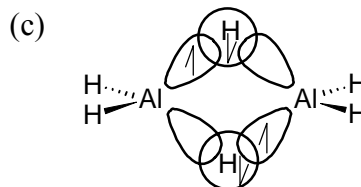
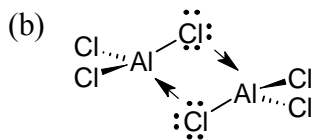
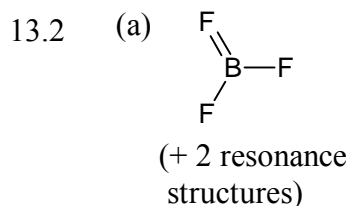
Row 2: This one cannot really be done. The solution manual claims BCl_3 because B is more electronegative and has a greater formal oxidation state, both of which are unconvincing to me.

Row 3: After reaction, the product of the *tert*-butyl-substituted boron will be less stable (due to steric crowding at the B), therefore it is the weaker acid.

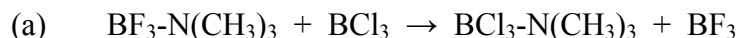
(b) Row 1: These are essentially the same.

Row 2: 2-methylpyridine will have a greater steric footprint than 4-methylpyridine, therefore the latter is the stronger base.

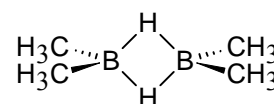
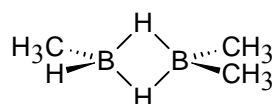
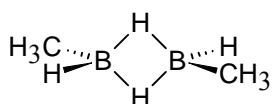
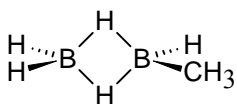
4.29 Fitting trimethylamine and trimethylboron together has a much greater steric problem than any of the others, so it causes an anomaly in the enthalpies.



13.3 This question is non-sensical unless you read ahead to the uses – *i.e.* we know that BF_3 is always weaker than BCl_3 , but BCl_3 is only stronger than $AlCl_3$ for hard bases (while $AlCl_3$ is stronger toward soft bases). Looking ahead, we see that the bases in question are N and C-based, so probably they are harder, thus BCl_3 is the strongest base. We cannot tell if $AlCl_3$ is next or if BF_3 is next.



13.p1 The information given implies that H can form banana bonds and BH₃ cannot. Therefore, the banana bonds will need to be made of H atoms and the CH₃ groups will have to be terminal. The structures are probably:

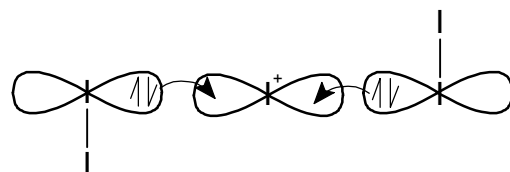


trans shown, could also be *cis* or *gem* (same C)

13.p6 You'll find the answers in the paper – you can access this through our library website.

16.3 It is the polarity of the X-H bond that gives rise to hydrogen bonding, so O-H is more polar than S-H, so the O-H...S should be the stronger hydrogen bond.

17.p4 This question is similar to the question posed in Experiment 4 – referring to catenating iodine. In this case, the I⁺ is the middle atom, with I₂ acting as a Lewis base and coordinating to it. Recall that the larger the atom, the less *sp*-hybridization occurs, so the lone pairs are *p*-orbitals (and the empty orbital on I⁺ is also a *p*-orbital, hence the 180° orientation of the two I₂s).



18.1 $K.E. = \frac{1}{2}mv^2$, and all gasses in the atmosphere at a given temperature will have the same K.E. Therefore He (and H₂, the most abundant molecule in the universe), being the lightest gasses are also moving the fastest, and in fact a significant proportion of these gasses at any given time can reach escape velocity and are therefore lost into space. (the lightest common gas in terrestrial bodies is methane, *e.g.* in the atmosphere of Titan).