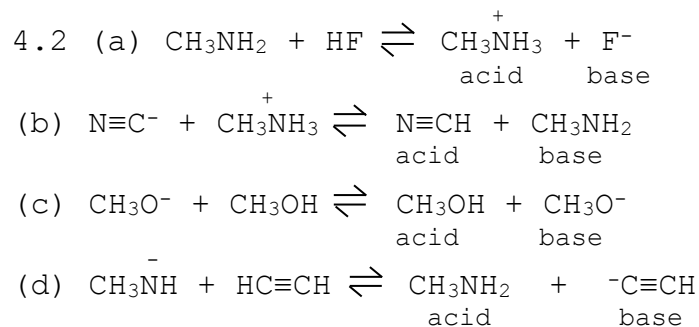
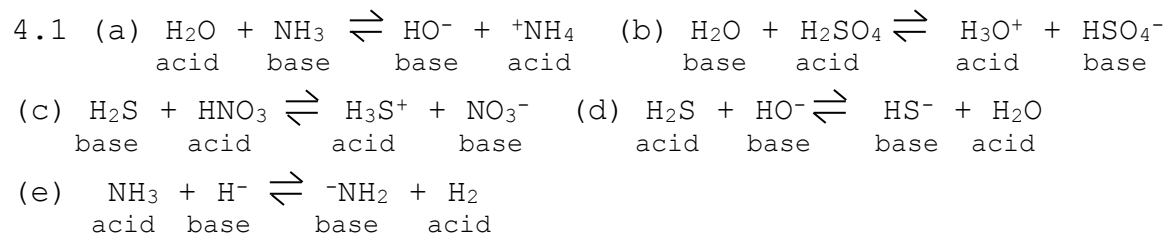


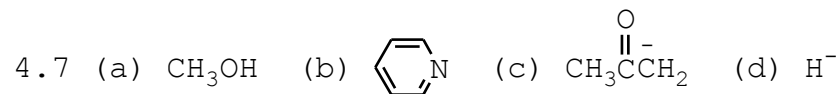
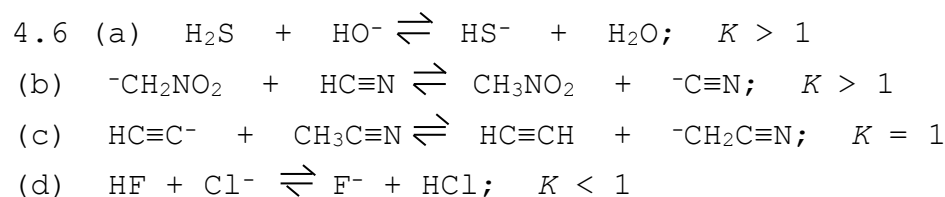
Answers to Puzzles of Chapter 4
Acids and Bases



- 4.3 (a) conj. acid $\text{}^+\text{NH}_4$; conj. base $\text{}^-\text{NH}_2$ (b) no conj. acid; conj. base NH_3
 (c) conj. acid NH_3 ; conj. base HN^{2-} (d) conj. acid CH_3OH_2^+ ; conj. base CH_3O^-
 (e) conj. acid H_2O ; conj. base O^{2-} (f) conj. acid H_4O^{2+} ; conj. base H_2O
 (g) no conj. acid; conj. base $\text{}^-\text{CH}_3$ (h) conj. acid CH_4 ; conj. base H_2C^{2-}
 (i) no conj. acid; conj. base CH_2 (j) conj. acid H_2Cl^+ ; conj. base Cl^-
 (k) conj. acid HBr_2^+ ; no conj. base (l) conj. acid $\text{CH}_3\text{-CH}_2^+$; conj. base $\text{}^-\text{CH}=\text{CH}_2$

- 4.4 (a) HNO_3 is the stronger acid (b) H_3O^+ is the stronger acid (c) NH_3 is the stronger acid
 (d) H_2S is the stronger acid

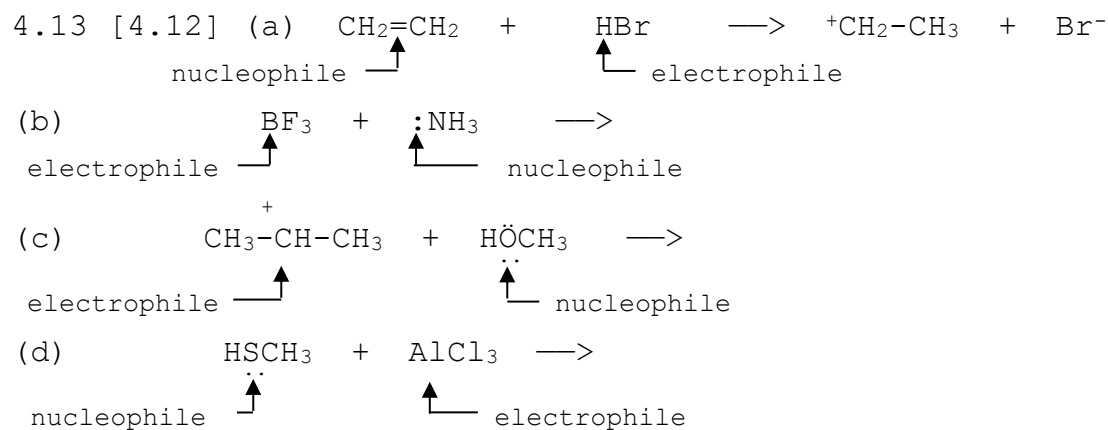
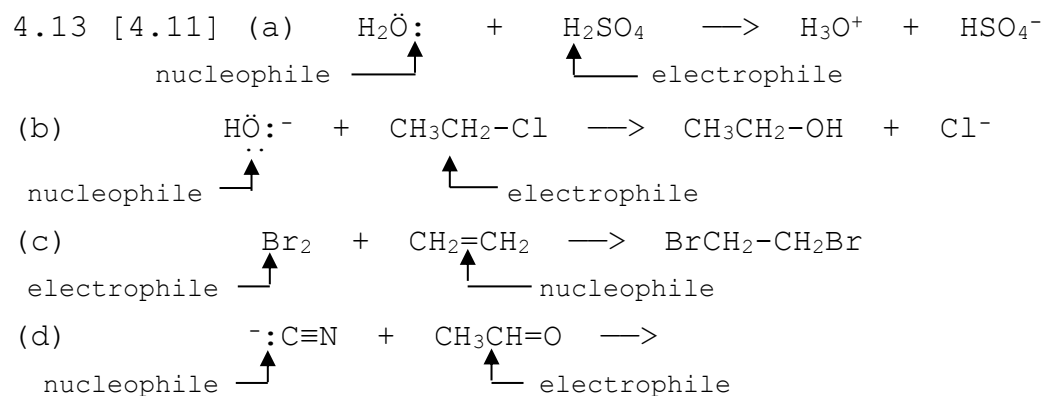
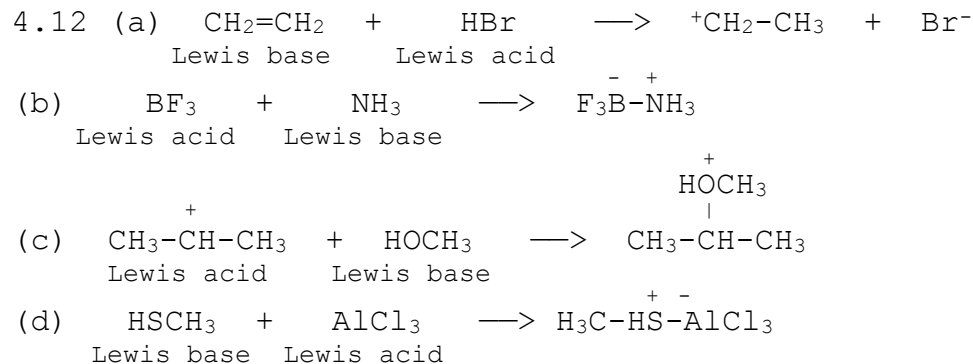
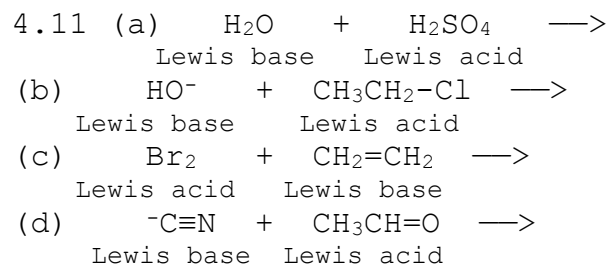
- 4.5 (a) CH_3O^- is stronger base (b) CH_3NH_2 is stronger base (c) F^- is stronger base
 (d) H_2N^- is the stronger base



- 4.8 (a) HBr (b) $\text{C}_6\text{H}_5\text{NH}_2$ (c) CH_3OH (d) $\text{HC}\equiv\text{N}$

- 4.9 (a) HNO_3 , HNO_2 , H_3O^+ are strong acids; H_2S is borderline
 (b) CH_3O^- , CH_3NH_2 , HO^- , H_2N^- are strong bases

- 4.10 (a) No, its $K_a < 10^{-7}$ (b) No, without a lone pair or $\text{C}=\text{C}$ it's not a base at all



- 4.14 (a) Be^{2+} is harder because Be is smaller than Mg.
 (b) Mg^{2+} is harder because it has more charge.
 (c) BF_3 is harder because EN F's put extra δ^+ on B.
 (d) CH_3F is harder because more EN F puts larger δ^+ on C.
 (e) CH_3COCl is harder because EN O puts larger δ^+ on C.

4.15 (a) Cl^- is harder because it is smaller. (b) $\text{N}(\text{CH}_3)_3$ is harder because N is smaller than P.

(c) HO^- is harder because it has more charge. (d) H_2O is harder because O is smaller than N.

4.16 Of course, compare conjugate bases.

In basicity: $\text{HO}^- > \text{HS}^- > \text{HSe}^-$ because in hardness: $\text{O} > \text{S} > \text{Se}$ and as hardness \uparrow , ability of base e's to pluck hard H^+ \uparrow . So in acidity: $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$.

4.17 Of course, compare conjugate bases.

In basicity: $^-\text{SiH}_3 > ^-\text{PH}_2 > ^-\text{SH} > ^-\text{Cl}$ because in EN: $\text{Si} < \text{P} < \text{S} < \text{Cl}$ and as EN \uparrow , stability of base e's \uparrow . So in acidity: $\text{SiH}_4 < \text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$.

4.18 H on O is most acidic because its conjugate base's base e's are stablest on most EN O atom.

4.19 Of course, compare conjugate bases.

In basicity: $^-\text{O}_2\text{C}-\text{CO}_2\text{H} < ^-\text{O}_2\text{C}-\text{CO}_2^-$ because the 2nd negative charge repels and destabilizes the base e's of the 2nd base. So in acidity: $\text{HO}_2\text{C}-\text{CO}_2\text{H} > \text{HO}_2\text{C}-\text{CO}_2^-$

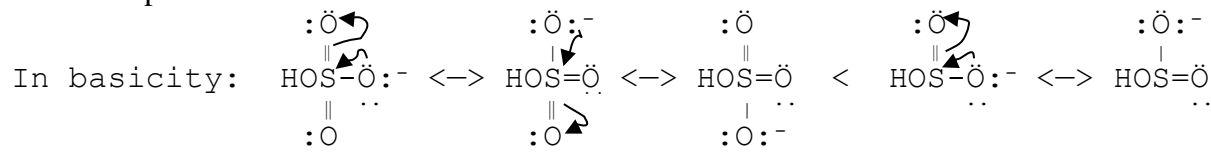
4.20 In basicity: $^-\text{O}_2\text{CCH}_2\text{CHCO}_2\text{H} > \text{HO}_2\text{CCH}_2\text{CHCO}_2^-$ because the $^+\text{NH}_3$ stabilizes the closer base e's more than the farther ones. Therefore the $-\text{CO}_2\text{H}$ H closer to the $^+\text{NH}_3$ is abstracted first.

4.21 (a) In basicity: $\text{F}-\text{O}^- < \text{Cl}-\text{O}^- < \text{Br}-\text{O}^- < \text{I}-\text{O}^-$ because the most EN F puts the most δ^+ on the O, which most attracts and stabilizes the base e's.

So in acidity: $\text{FOH} > \text{ClOH} > \text{BrOH} > \text{IOH}$.

(b) In basicity: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ because F is hardest and base e's on a harder atom are more able to pluck a hard H^+ . So in acidity: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

4.22 Compare the bases themselves.

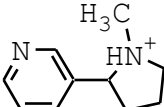


because the 1st base has more resonance forms that stabilize the base e's.

4.23 $K_a \cong 2 \times 10^{-5}$, like that of $\text{H}_3\text{CCO}_2\text{H}$.

4.24 (a) Ethyne is much more acidic. In basicity: $\text{HC}\equiv\text{C}^- < ^-\text{CH}_3$ because 3 (not 1) repelling electron pairs at 109° (not at 180°) destabilize the base e's in $^-\text{CH}_3$.

(b) $\text{HC}\equiv\text{N}$ is much more acidic. In basicity: $\text{HC}\equiv\text{C}^- > \text{HC}\equiv\text{N}^-$ because the more EN N stabilizes the base e's more than the C does.

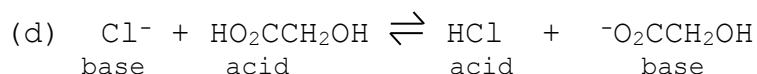
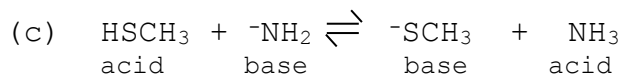
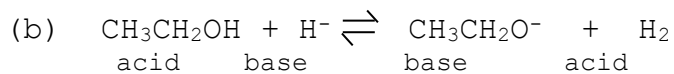
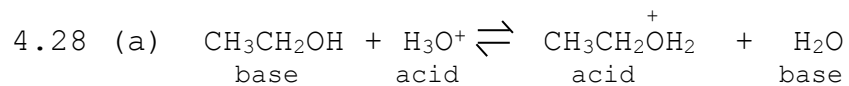
4.25  because the sp^3 N is more basic than the sp^2 N.

4.26 (a) $\text{HO}^- + ^+\text{NH}_4 \longrightarrow \text{H}_2\text{O} + \text{NH}_3$ is faster than:

$\text{HS}^- + ^+\text{NH}_4 \longrightarrow \text{H}_2\text{S} + \text{NH}_3$ because HO^- is harder than HS^- and reacts better with the hard H^+ of $^+\text{NH}_4$

(b) $\text{HS}^- + \text{H}_3\text{C}-\text{Br} \longrightarrow \text{H}_3\text{C}-\text{SH} + \text{Br}^-$ is faster than:
 $\text{HO}^- + \text{H}_3\text{C}-\text{Br} \longrightarrow \text{H}_3\text{C}-\text{OH} + \text{Br}^-$ because softer nucleophile HS^- reacts better with the soft electrophile $\text{H}_3\text{C}-\text{Br}$.

4.27 C is softer than the smaller O and so will better attract the soft, fourth-row iron.



4.29 (a) e.g., Br_2 , no H (b) e.g., BH_3 , no lone pair or C-C π bond

(c) Na, no H, lone pair, or C-C π bond

4.30 (a) $\text{CH}_3\text{SO}_3\text{H}$; both are strong (b) $\text{CH}_3\text{CH}_2\text{SH}$; $\text{CH}_3\text{CH}_2\text{SH}$ is a borderline strong acid

(c) $\text{CH}_3\text{CH}_2\text{NH}_2$; neither is a strong acid

4.31 (a) NH_3 is stronger base; HOCO_2^- is stronger acid

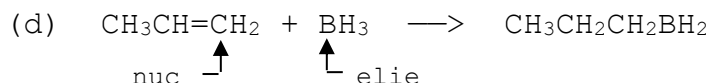
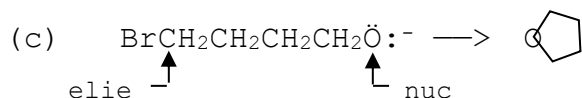
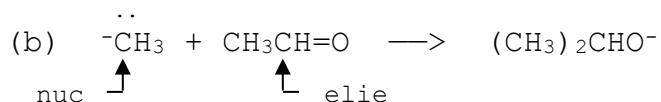
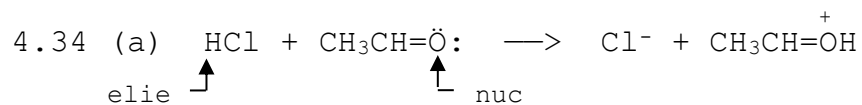
(b) H_2PO_3^- is stronger base & stronger acid (c) CH_3OH is stronger base & stronger acid

4.32 (a) $\longrightarrow \text{CH}_3\text{C}\equiv\text{C}^- + \text{C}_6\text{H}_5\text{CH}_3$; products (b) $\longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$; reactants

(c) $\longrightarrow \text{C}_6\text{H}_5\text{NHCH}_3 + \text{CH}_3\text{CH}_2\text{OH}_2^+$; reactants

4.33 (a) No, because methanol's $K_a \cong K_a$ of water, the conjugate acid of hydroxide ion.

(b) A better base would be a stronger base, such as $^-\text{NH}_2$.



4.35 The 1st reaction is most likely to occur because both of its products are fairly stable, octet-satisfied molecules. The product of the second reaction has too many electrons around its oxygen. The hydride ion produced in the third reaction is a very strong, unstable base.

4.36 (a) 1st reaction is faster because the C^- has more negative charge and so is harder and more attractive to a hard H^+ .

- (b) 1st reaction is faster because P is larger, softer, and more attractive to soft electrophile.
 (c) 1st reaction is faster because C is larger, softer, and more attractive to soft electrophile.

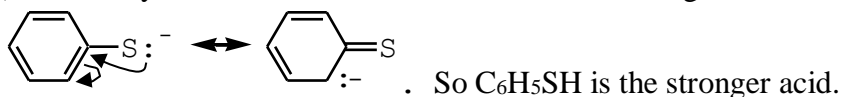
4.37 (a) In basicity: $^-:\text{NHCH}_3 > ^-:\text{P}(\text{CH}_3)_2$ because the base e's on the smaller, harder N react better with hard H^+ . So $\text{PH}(\text{CH}_3)_2$ is the stronger acid.

(b) In basicity: $:\text{SHCH}_3 > \text{HCl}$: because more χ Cl stabilizes the base e's more. So H_2Cl^+ is the stronger acid.

(c) In basicity: $\overset{+}{\text{O}}_2\text{NCH}_2\overset{-}{\text{C}}\text{O}_2^- < \text{CH}_3(\text{CH}_2)_3\overset{-}{\text{C}}\text{O}_2^-$ because N^+ attracts & stabilizes base e's. So $\text{NO}_2\text{CH}_2\text{CO}_2\text{H}$ is the stronger acid.

(d) In basicity: $:\text{NH}_2\text{CH}_2\text{CH}_2\text{OH} < :\text{NH}_3\text{CH}_3$ because EN O puts a δ^+ on its C, which attracts & stabilizes the base e's. So $^+\text{NH}_3\text{CH}_2\text{CH}_2\text{OH}$ is the stronger acid.

(e) In basicity: $\text{C}_6\text{H}_5\text{S}^- < \text{CH}_3\text{S}^-$ because benzene ring stabilizes the base e's by resonance:



(f) In basicity: $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2^- \cong \text{CH}_3\text{CH}_2\text{CO}_2^-$ because benzene ring can't affect base e's. So both acids are about equally strong.

4.38 (a) In basicity: $\text{CH}_3\overset{-}{\text{O}}\text{H} > \text{CH}_3\text{F}$: because base e's are stabler on more χ F.

(b) In basicity: $\text{CH}_4 < :\text{NH}_3$ because CH_4 has no base e's.

(c) In basicity: $\text{CH}_3\overset{-}{\text{C}}\text{O}_2^- > \text{ClCH}_2\overset{-}{\text{C}}\text{O}_2^-$ because Cl puts a δ^+ on its C, which attracts & stabilizes base e's.

(d) In basicity: $\text{ClCH}_2\overset{-}{\text{C}}\text{O}_2^- > \text{Cl}_2\text{CH}\overset{-}{\text{C}}\text{O}_2^-$ because 2 EN Cl's put a larger δ^+ on their C, which attracts & stabilizes the base e's more.

(e) In basicity: $\text{ClCH}_2\overset{-}{\text{C}}\text{O}_2^- < \text{ClCH}_2\text{CH}_2\overset{-}{\text{C}}\text{O}_2^-$ because the 1st base's Cl puts a δ^+ closer to the base e's, which attracts & stabilizes them more.

(f) In basicity: $^-:\text{CH}_3 > ^-:\text{SiH}_3$ because the base e's on the smaller, harder C react better with a hard H^+ .

4.39 (a) K_a of $\text{CH}_3\text{CH}_3 \cong K_a$ of $\text{CH}_4 = 10^{-50}$ (b) K_a of $\text{CH}_3\text{SH} \cong K_a$ of $\text{H}_2\text{S} = 1 \times 10^{-7}$

(c) K_a of $\text{CH}_3\text{CH}_2\text{CO}_2\text{H} \cong K_a$ of $\text{CH}_3\text{CO}_2\text{H} = 2 \times 10^{-5}$

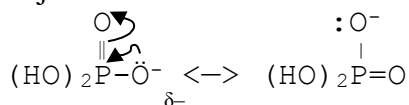
4.40 (a) Both acids react favorably because both have K_a 's $> K_a$ of H_2O , conjugate acid of HO^- .

(b) Benzoic acid reacts favorably because it has a $K_a > K_a$ of H_2CO_3 , conjugate acid of HCO_3^- .

4.41 (a) F^- forms stronger H "bond" with CH_3OH because the small H is hard and F^- is harder than Cl^- .

(b) In methanol F^- is a weaker nuc because CH_3OH solvates it more strongly with H "bonds". Yet in acetone (propanone) F^- is a stronger nuc because it cannot be solvated with H bonds and is a stronger (harder) base than Cl^- .

4.42 (a) 2 major resonance forms stabilize the base e's of its conjugate base:



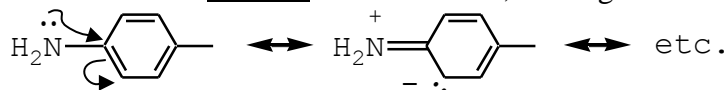
(b) In basicity: $\text{H}_2\text{O}_3\text{P}-\overset{-}{\text{O}} > \text{HO}_3\text{S}-\overset{-}{\text{O}}$ because $\text{H}_2\text{O}_3\text{P}-\overset{-}{\text{O}}$ has fewer (2 vs. 3) major resonance forms stabilizing base e's and because P, less EN than S, puts a bigger δ^- on the O, repelling & destabilizing base e's more.

4.43 (a) Both S & O have lone pairs & are nucleophiles.

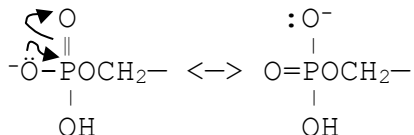
(b) The harder O bonds to the harder Cu of CuCl_2 . The softer S bonds to the softer Pt of PtCl_2 .

4.44 H_2SO_4 can protonate a lone pair on O, N, or S and so make their compounds ionic & polar enough to dissolve in polar H_2SO_4 .

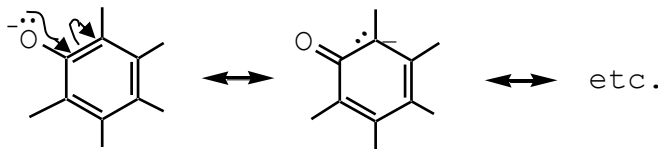
4.45 Resonance stabilizes the base e's on the other N, making it less basic:



4.46 The 2 equivalent O's on the P have the most acidic H's because resonance in the conjugate base stabilizes the base e's:



4.47 Vitamin E is more acidic because removing the proton from its O gives a conjugate base whose base e's are stabilized by resonance:



4.48 In $:\text{N}\equiv\text{N}:$ the sp N's have only 1 e^- pair repelling the base e's. Also N_2 has no δ^- to repel the base e's.

4.49 (a) Yes. E.g. H_2O (b) Yes. E.g. NH_3 (c) Yes. E.g. HSO_4^-

(d) If H-Z: is a strong acid, then $:\text{Z}:^-$ must be a weak base. But if H-Z: is a strong base, then $:\text{Z}:^-$ must be an even stronger base because of its -. This contradicts $:\text{Z}:^-$ being a weak base. So a strong acid cannot be a strong base.

6/10