Course 343 Lecturer Sam Gellman

Day Monday Date 9-19-16

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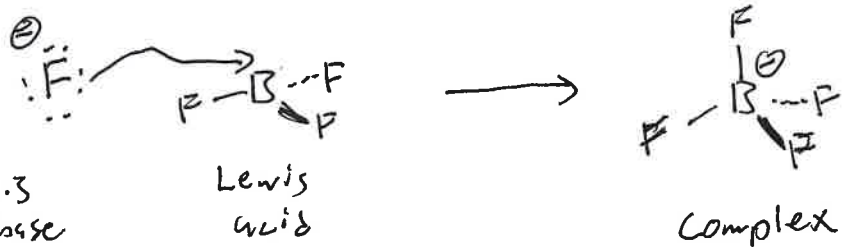
Recall: Acid-base chemistry (Chap. 3)

Rec. problems: 1-5, 7-12, 16, 19, 27, 32-36, 37a, 40
44, 47, 52-55

1. Proton transfer ($H^{\oplus}$) - Brønsted acids and bases
2. Lewis acids and bases; curved arrows to indicate e^- pair movement

Ex:



Lewis base — Lewis acid — Complex

Acid strength - pK_a scale

$$H\text{-}A + H_2O \rightleftharpoons A^{\ominus} + H_3O^{\oplus}$$

$$K_{eq} = \frac{[A^{\ominus}][H_3O^{\oplus}]}{[HA][H_2O]} \rightarrow K_a = \text{"acid dissociation constant"}$$

$$K_a = \frac{[A^{\ominus}][H_3O^{\oplus}]}{[HA]} = K_{eq}[H_2O] \quad \text{----> to make things easier, use log scale}$$

$$pK_a = -\log K_a$$

Stronger acid $\Leftrightarrow$ smaller pK_a

Look at Table 3.1

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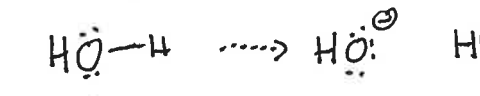
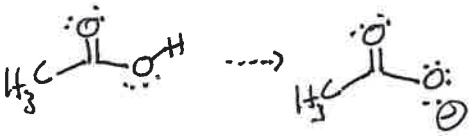
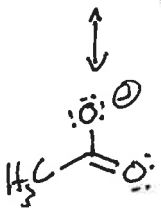
Examples!

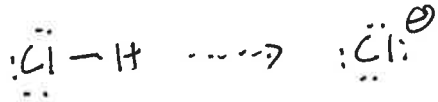


$pK_a \sim 16$



$pK_a \sim 5$ — 11 orders of magnitude more acidic than H_2O.





$pK_a \sim -6$

expected to know pK_a values from Table 3.1 for other functional groups.

use pK_a information to reason about chemical phenomenom.

For example:

1. Predict which side favored acid-base equilibria

(weaker acid/stronger base pair always favored)

$pK_a \sim 16$

Favored side of equilibrium

$pK_a \sim 5$

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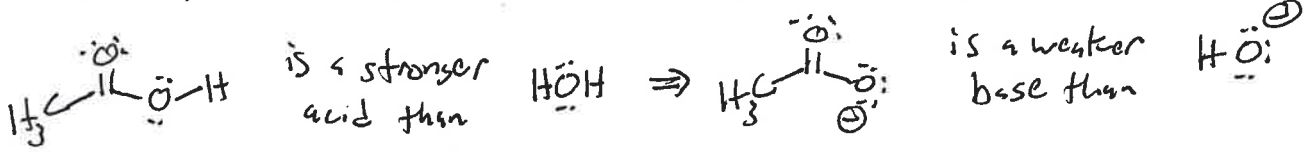
2. Use pka values to assess relative basicities.



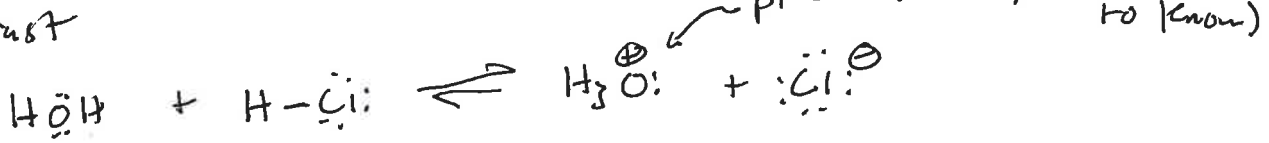
"Amphoteric acids" – multiple protons

Potential sources of confusion, be careful in questions involving these species and in your own communications about them.

Ex:

→ H_2O acting as acid, pka ~16

Contrast



→ H_2O acting as a base

Relationships between molecular structure and Brønsted acidity.

Common trends...

1. Periodic trends... other factors being ~~about~~ equivalent.
   acidity generally increases going ~~right~~ left to ~~left~~ right along a row.

	H_3C-H	H_2N-H	$HO-H$	$F-H$
* pka values	255	~35	~16	~3

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2) Charge effects - cationic acids tend to be more acidic than analogous neutral acids.

Ex: $H_3\overset{\oplus}{N}-H$ pKa ~9

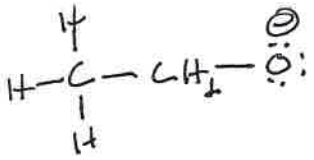
H_2N-H ~35

3) Polar substituent effects - electronegative substituents can significantly effect pKa.

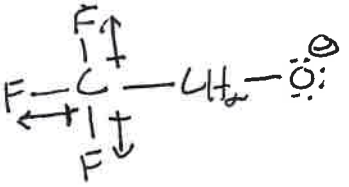
$CH_3CH_2\ddot{O}-H$ vs. $F_3CCH_2\ddot{O}-H$

pka ~16 (pka ~12) ← not expected to know this specific example

Consider the conjugate bases, focus on substituent effects on charge.



vs.



Stronger base

Sucking of negative charge towards the fluorines better accomodates the negative charge on oxygen, making it the ~~best~~ weaker base