I. What do you know already about acids and bases?

Acids: sour taste (vinegar, acetic acid, soda, phosphoric acid)  
corrosive (HCl, H₂SO₄ evolves H₂ on metal surfaces – remember the reaction from Inorg.Chem.)  
acid rains (environmental impact)

Bases: bitter taste (swiss chard with high oxalic acid content, baking soda, organic acid salts)  
slippery (a drop of dilute NaOH solution on your finger – no fingerprint)  
alkali soils (white salt flowers on the ground)

Acid + Base = flavorless, non-reactive mixture ⇒ neutralized

II. Acid/Base theories: (microscopic consideration – what happens at the level of molecules)

a) Lavoisier (18th century): studying sulfuric and other oxoacids ⇒ oxygen is acid “generator”
b) Davy (1810): studying inorganic acids ⇒ HCl is a strong acid
c) Arrhenius (1880): studying electrolytes, ionic dissociation (remember bp increase, fp depression, osmosis)  
acid: dissociates to H⁺ neutralization
bases: dissociates to OH⁻ H⁺ + OH⁻ → H₂O

problems: bubble NH₃ through HCl ⇒ neutralization without presence of OH⁻  
HCl in H₂O does not give H⁺ → proton transfer to give hydronium ion H₃O⁺

d) Brønsted-Lowry (1923):  
acid: donates H⁺ definition by
base: accepts H⁺ proton transfer reactivity

in general:  
HA + H₂O → A⁻ + H₃O⁺  
acid base conj.base conj.acid  
BUT, also present
HA + A⁻ → HA + A⁻  
which is trivial
H₃O⁺ + H₂O → H₃O⁺ + H₂O  
as well as most importantly
H₂O⁺ + A⁻ → HA + H₂O  
acid base conj.base conj.acid

the possibility of forward and backward reaction taking place leads to EQUILIBRIUM

remember definitions for chemical equilibrium: ΔG = 0, K can be defined, forward rate = reverse rate

consider an example from above:

\[
\begin{align*}
\text{HCl}_{(g)} + \text{NH}_3_{(aq)} & \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{Cl}^-_{(aq)} \\
\Delta H^0 & = -92 \text{ kJ/mol} \\
\Delta S^0 & = -80 \text{ J/mol K} \\
\Delta G^0 & = -132 \text{ kJ/mol} \\
\Delta F^0 & = -167 \text{ kJ/mol}
\end{align*}
\]

exothermic reaction, spontaneous at 25 °C; but working against exothermicity

\[
\Delta G^0 = -RT \ln K; \ K = e^{35.5} \rightarrow \text{shifted far to the right side} \quad K = [\text{NH}_4^+] [\text{Cl}] / [\text{NH}_3][\text{HCl}]
\]
bimolecular for a proton-transfer reaction, donor and acceptor need to collide for exchanging protons.

**problems:**
- acidic behavior of transition metal ions, Cu$^{2+}$, Fe$^{3+}$, etc. → no proton transfer
- alkaline/basic behavior for AlCl$_3$, BF$_3$
- “non-aqueous chemistry”, ionic liquids

### III. Lewis acid/base concept:

- **acid:** electron-pair acceptor
- **base:** electron-pair donor
  - forming a dative covalent bond between an acid and a base

\[
\text{H}_3\text{N} + \text{BF}_3 \rightarrow \text{H}_3\text{N}-\text{BF}_3 \quad (\text{N lone-pair is shared by N and B})
\]

Base

Acid

**remember from Inorg.Chem.:**
\[
\text{CuCl}_2 + 6 \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 2\text{Cl}^- + 6 \text{H}_2\text{O} \rightarrow [\text{Cu(OH}_2]^2+ + 2 \text{Cl}^{-}
\]

- competition among Lewis basis (OH$^-$, Cl$^-$, ... ) for the Lewis acid (Cu$^{2+}$)

#### Structure and bonding in molecules influences the acid strength

- **H – A → H$^+$ + A$^-$**
- balancing energy: breaking H-A bond (heterolitic cleavage)
- solvating the ions (remember dipole/charge interaction is about 50-70 kJ/mol)
- strength of the H-A bond determines the acid strength

a) Organic acids: remember from Org.Chem. classes - inductive effects, bond polarization, partial charges
- H$_2$C-C(O)-O-H due to carbonyl, O-H bond is weak → behaves as acid
- H$_3$C-H$_2$C-O-H methyl group is electron donor, O-H bond is strong → protonsation of OH can lead to activation, H$_2$O elimination, carbocation formation
- F$_3$C-C(O)-O-H strong electron withdrawing by F$_3$C → as strong as sulfuric acid

b) Inorganic acids: bond strength: HF > HCl > HBr > HI (remember orbital energy + orbital overlap)
- acidity: HF < HCl < HBr < HI

c) Inorganic oxoacids: compare H$_2$SO$_3$ and H$_2$SO$_4$, which is stronger?
- as the number of O atoms increases the electron withdrawing of the central atom saturates and more polarized the H-O bonds get