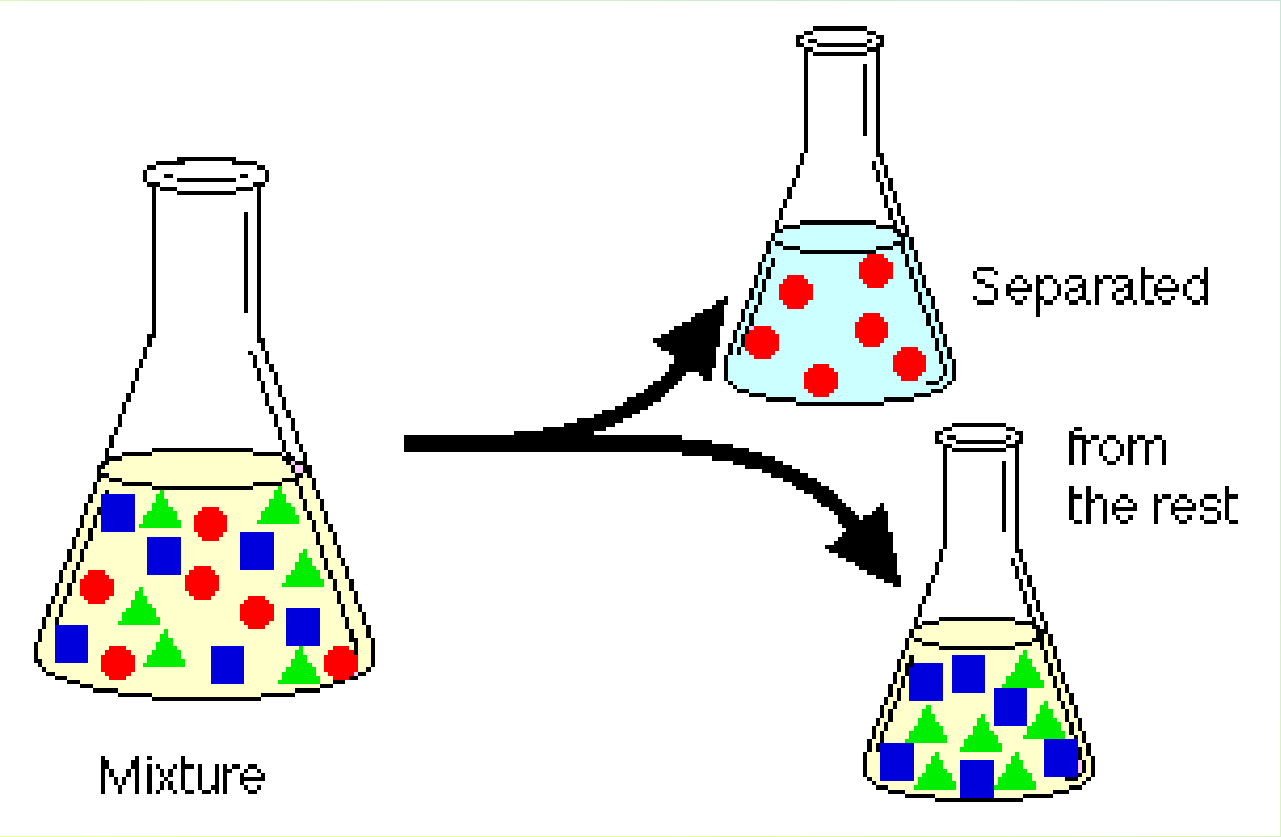
THE FAR SIDE By GARY LARSON

"Mr. Osborne, may I be excused? My brain is full."

Solvent extraction

What is liquid-liquid extraction?

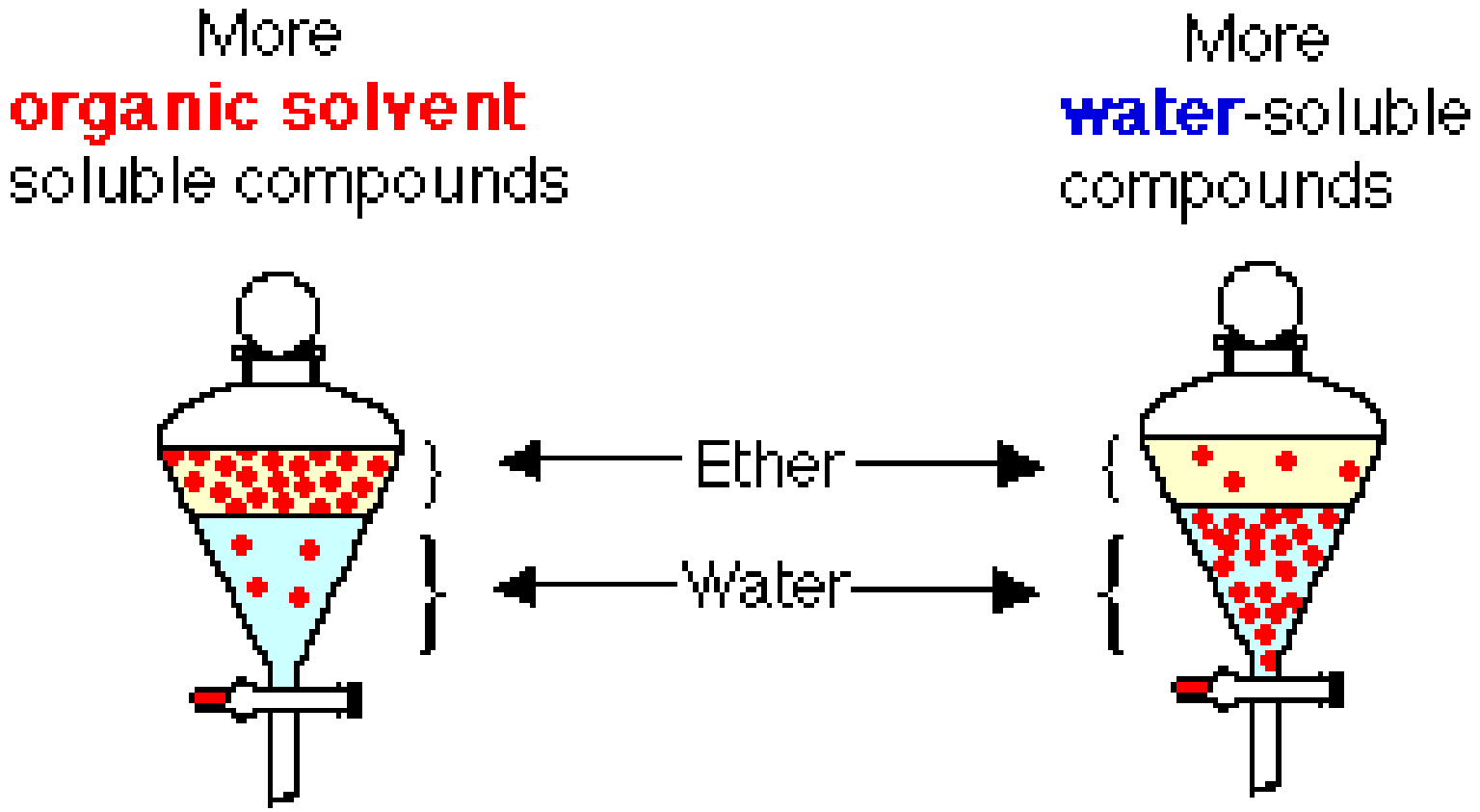
Liquid-liquid extraction is a useful method to separate components (compounds) of a mixture.

- 

Distribution coefficient "K"

- When shaken, with two immiscible solvents, the compound will distribute itself between the two solvents.
  Normally one solvent is **water** and the other solvent is **a water-immiscible organic solvent**.

  Most organic compounds are more soluble in organic solvents, while some organic compounds are more soluble in water.


More
organic solvent
soluble compounds
More
water-soluble
compounds
Ether
Water

- **At a certain temperature, the ratio of concentrations of a solute in each solvent is always constant.**

$$K = \frac{\text{concentration in solvent}_2}{\text{concentration in solvent}_1}$$

- This ratio is the

distribution coefficient, K_D or partition coefficient.

(solvent1 and solvent2 are immiscible liquids)

Extraction efficiency

$$\frac{\text{mass}_{\text{organic phase}}}{\text{mass}_{\text{aqueous phase}}} = \frac{M_{org} V_{org}}{M_{aq} V_{aq}}$$

Fraction remaining in aqueous phase after one extraction:

$$q = \frac{M_{aq} V_{aq}}{M_{aq} V_{aq} + M_{org} V_{org}} = \frac{V_{aq}}{V_{aq} + K V_{org}}$$

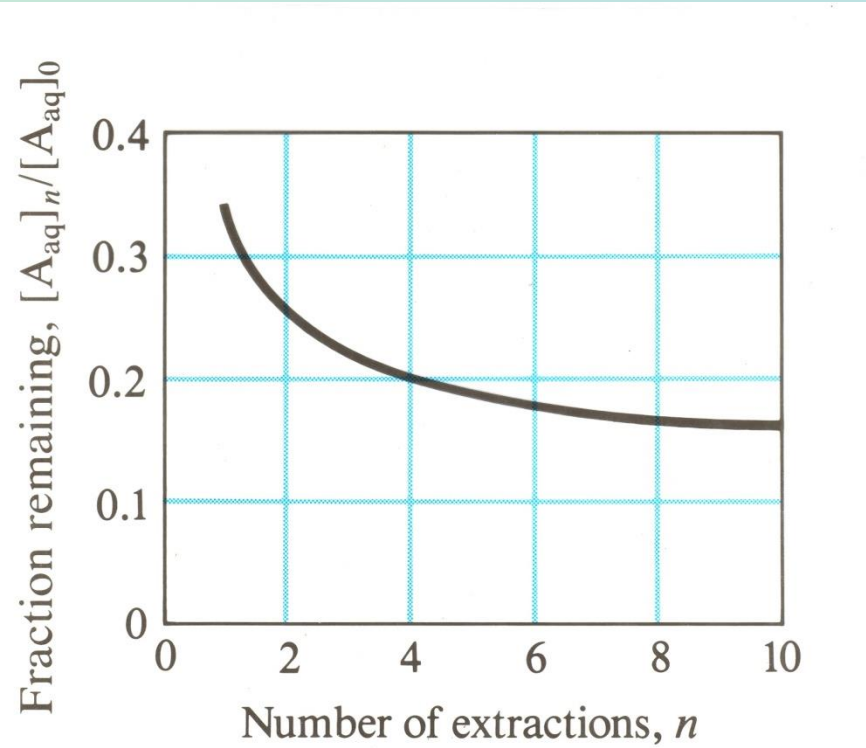
- **After n extractions with V_{org}, the fraction remaining in the aqueous phase is:**

$$q^n = \left(\frac{V_{aq}}{V_{aq} + KV_{org}}\right)^n$$

Successive extractions

- Extracting with the same amount of solvent but divided into several smaller fractions, is more efficient.

- Usually don't do more than three successive extraction



K = 2,

Vaq = 100 mL,

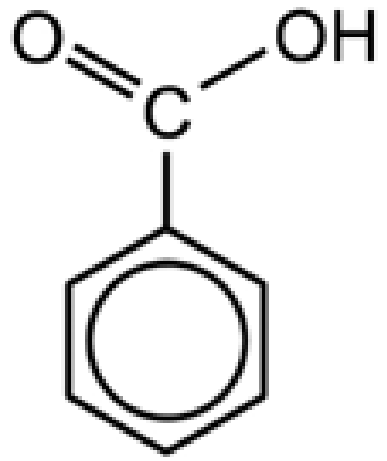
Vorg = 100/n mL.

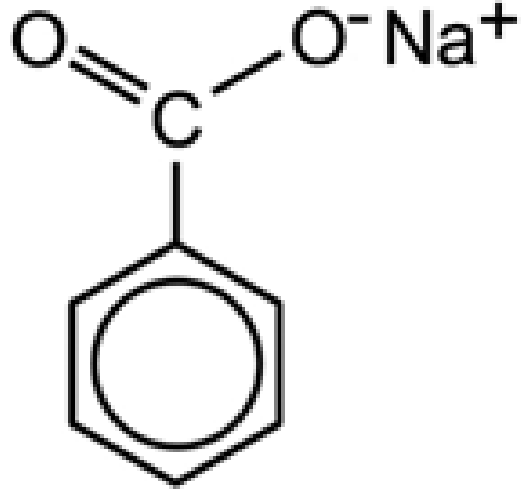
Some organic compounds can be made water-soluble.

- Compounds belonging to the following solubility classes can be converted to their **water-soluble salt form**.
- Organic Acids and Organic Bases
- **Organic acids** include **carboxylic acids (moderately weak organic acids)** and **phenols (weak organic acids)**.
- **Bases include amines**

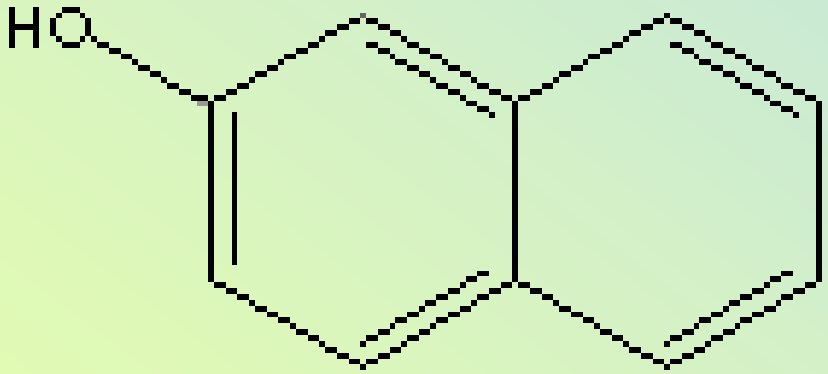
To a first approximation, in dilute solution, K_D is independent of concentration.

- K_D pertains to a single species
- Doesn't include products of side reactions
- Consider the distribution of benzoic acid between benzene and water

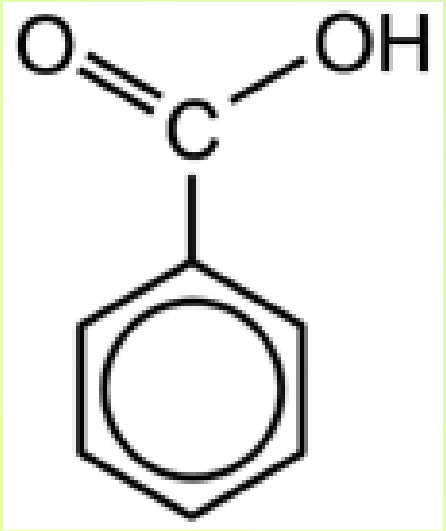




Separating species



B-naphthol



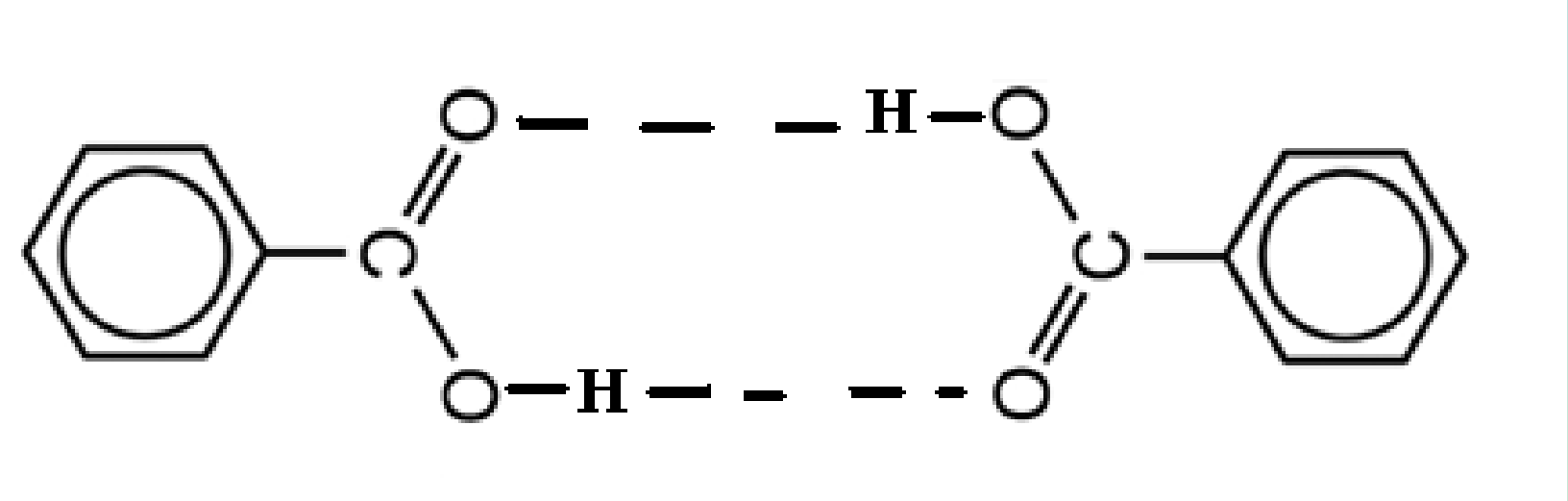
Benzoic acid

- pH < 2 Both non-ionic, both will transfer to benzene.

- pH > 5 Benzoic acid is deprotonated and stays in water
- □-naphthol still transfers to benzene

- pH 11 Both dissociate and both stay in water.

Some dimerizes in the organic phase



Each species has own K_D

But we are interested in total amount extracted

$$D = \frac{\text{Total benzoic in organic phase}}{\text{Total benzoic in aqueous phase}}$$

$$D = \frac{[HBz]_{org} + 2[(HBz)_2]_{org}}{[HBz]_{aq} + [Bz^-]_{aq}}$$

D is the Distribution ratio

- **Substitute**:

$$[Bz^-] = K_a \frac{[HBz]}{[H^+]},\ K_D = \frac{[HBz]_{org}}{[HBz]_{aq}} \quad \text{and}$$

$$[(HBz)_2] = K_f [HBz]^2$$

then

$$D = \frac{K_D(1 + 2K_f[HBz])}{1 + \dfrac{K_a}{[H^+]}}$$

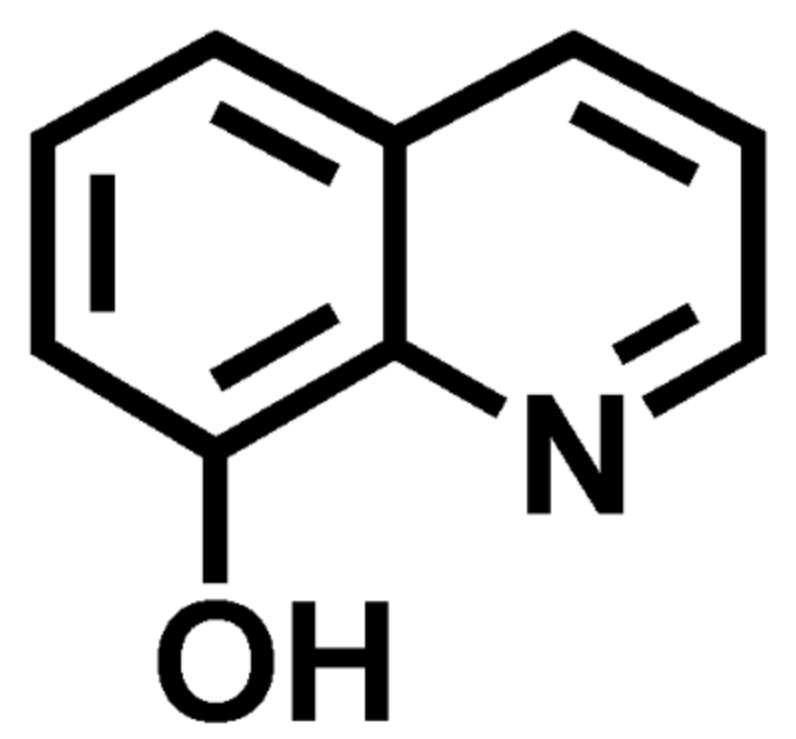
For a weak acid which doesn't dimerize – can simplify:

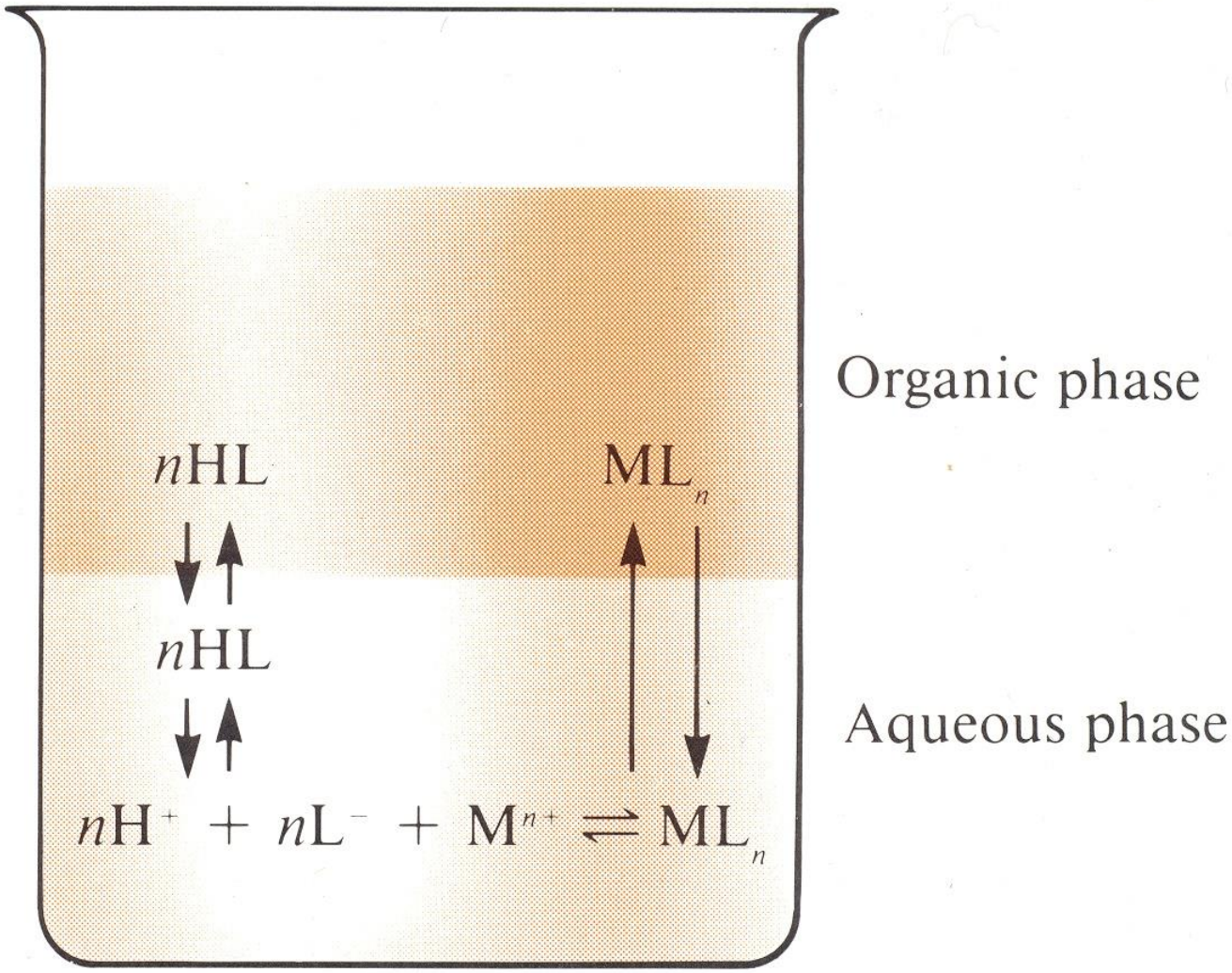
$$D = \frac{K_D}{1 + \frac{K_a}{[H^+]}}$$

Metal ion Extraction

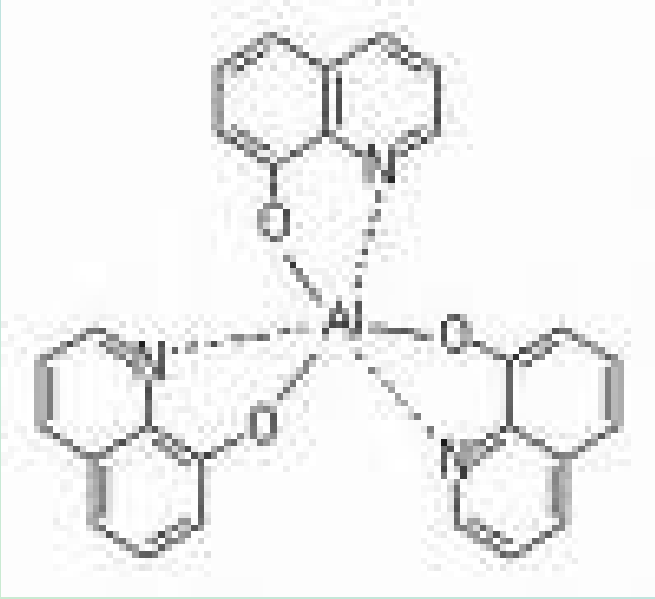
- Must create a neutral, hydrophobic complex to extract into an organic phase.
- We use chelating agents
- E.g. 8-hydroxy-quinoline

(oxine, 8-quinolinol)





Complex formation is pH dependent, but the stronger the complex (K_f), the lower the pH which can be used.



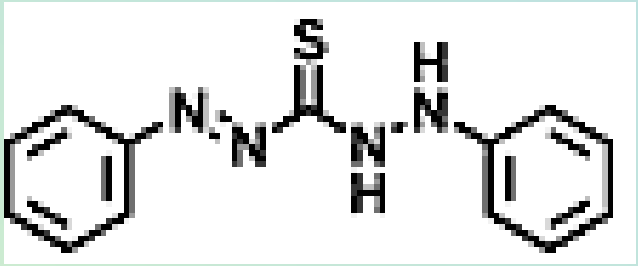
Neutral species are extracted

$Cu^{2+} + L^{2-} \Leftrightarrow CuL^0$

With Fe^{3+}, get $(FeL)^+$ or $(FeL_2)^-$

Therefore can separate Cu^{2+} from Fe^{3+}

- **Another important reagent for the solvent extraction of metal ions is dithizone, diphenylthiocarbazone.**

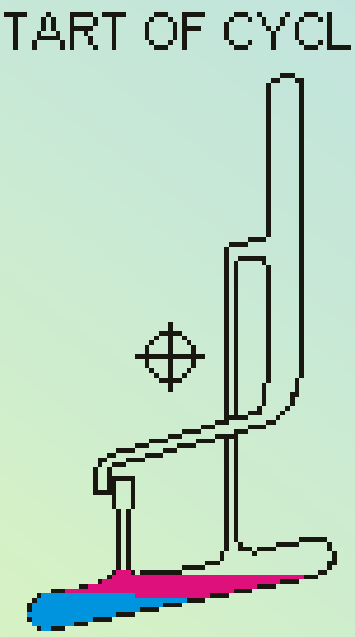


- Some salts form complexes (ion pairs) which can be extracted
- eg $[FeCl_4]^-H_3O^+$

Applications

- Separation – controlled by pH which controls ionization and complex formation
- Clean up before analysis
- Preconcentration: Extract from a large aqueous volume into a much smaller organic volume.

- Craig method: you want to separate two species by solvent extration but their K_Ds are not sufficiently different. So carry out a series of extractions:



Counter current extraction