For a solute, Z, in equilibrium exists between an aqueous and organic solvent:

\[ Z_{(2)} \cdot Z_{(1)} \]

At equilibrium, we have:

\[ K_P = \frac{[Z_1]}{[Z_2]} \]

This assumes ideal behavior at low concentrations. It actually results in a ternary system.

When dealing with aqueous species, the solute may exist in equilibrium with several other forms.

Example - a weak acid

\[ \text{HA} \quad \text{H}^+ + \text{A}^- \]

Due to competing equilibria, we define an alternate form of the partition coefficient:

\[ D_c = \frac{[\text{total Z}]_1}{[\text{total Z}]_2} = \frac{C_1}{C_2} \]

Total Z represents the total of all equilibrium forms of species Z.

This ratio is based on specific solution conditions such as pH.

\[ D_c = \frac{K_P[H^+]}{K_a[H^+]} \]

\[ \log D_c = (1) \]

A plot of \( \log D_c \) vs \( \log \text{pH} \) shows two regions.

1 - \( [H^+] >> K_a \), \( D_c \propto K_P \)

2 - \( D_c \) is pH dependent

Its best to hold pH and other factors constant.

\[ \log D_c = (2) \]

In the case of a weak acid, \( D_c \) is dependent on solution pH.

If \( K_P = [\text{HA}]_1 / [\text{HA}]_2 \)

and \( K_a = [H^+]_2 [A^-]_2 / [\text{HA}]_2 \)

then \( D_c = \frac{[\text{HA}]_1}{[\text{HA}]_2 + [A^-]_2} \)

\[ = \frac{[\text{HA}]_1}{K_P [\text{HA}]_1 + K_a [H^+]_2} \]

\[ = \frac{K_P[H^+]_2}{[H^+]_2 + K_a} \]

\[ \text{Obligatory derivation designed to impress you with how much I know. Do you really care about this?} \]

\[ D_c \]
The $D_c$ can be defined based on total equilibrium concentrations as:

$$D_c = \frac{C_1}{C_2}$$

where:
1 is the phase being extracted into
2 is the phase being extracted from

All solution conditions are assumed constant. Total solute amounts are based on solution volume.

The initial moles of solute is $C_0V_2$

so at equilibrium:

$$n_{\text{solute 1}} = C_1V_1$$
$$n_{\text{solute 2}} = C_2V_2$$

In terms of fractional amounts:

$$p = \text{fraction in 1} = \frac{C_1V_1}{C_1V_1 + C_2V_2}$$
$$q = \text{fraction in 2} = \frac{C_2V_2}{C_1V_1 + C_2V_2}$$

If we define the volume ratio ($V_R$) as

$$V_R = \frac{V_1}{V_2}$$

then

Amount extracted q = \frac{1}{D_cV_R + 1}

Amount remaining p = \frac{D_cV_R}{D_cV_R + 1}

To help keep things straight, let’s define some conditions for a single extraction or contact unit.

Most often, we are interested in extracting from an aqueous into an organic phase.

**organic phase**
- density $> 1.00$ g/ml - call it phase 1

**aqueous phase**
- density $\sim 1.00$ g/ml - call it phase 2

If the aqueous phase is what we are extracting from, then:

- $V$ - volumes, all must be in same units
- $C$ - total concentrations
- $C_1$ - organic concentration
- $C_2$ - aqueous concentration
- $C_0$ - initial concentration
Since $V_1 = V_2$, $V_R = 1$,

$$p = \frac{D_c V_R}{D_c V_R + 1} = \frac{3.0}{3.0 + 1} = \frac{3}{4}$$

$$q = \frac{1}{D_c V_R + 1} = \frac{1}{3.0 + 1} = \frac{1}{4}$$

$$%E = 100 \times p = 75\%$$

### Solute extraction

**Determining amounts**

We started with $1.00 \times 10^{-2} \text{ M}$ in 100.0 ml of the aqueous phase so:

$$n_T = (0.100 \text{ l})(1.00 \times 10^{-2} \text{ M}) = 1.00 \times 10^{-3} \text{ mol}$$

$$n_1 = 7.5 \times 10^{-4} \text{ mol} \quad M_1 = 7.5 \times 10^{-3}$$

$$n_2 = 2.5 \times 10^{-4} \text{ mol} \quad M_2 = 2.5 \times 10^{-3}$$

### Deviations from ideal behavior

Solutions can vary from ideal behavior either from the start or during an extraction.

Possible causes include:
- dissolution of one phase into the other
- solute saturation of a phase
- reaction of solute with a phase
- alteration of conditions like pH during an extraction.

You can end up with three types of behavior - **partition isotherms**:

- a - ideal behavior
- b - solute association, dimerization, etc.
- c - phase 1 is an absorbed phase. Approaching saturation

You must also remember that we assumed that activity and concentration were proportional.

We attempt to avoid problems by:
- Working at low concentrations
- Maintaining factors like pH as constants

We do our best to stay as close to ideal conditions as possible.
It is not always possible to quantitatively remove the solute using a single extraction.

Your options typically are to:

Increase the volume of the extracting solvent - not usually a good idea.
Use multiple extractions.

Total amounts extracted are the sum of all extractions so:

\[(p + pq + pq^2 + \ldots + pq^{n-1})C_0V_2 = (1-q^n)C_0V_2\]

or

\[1 - q^n = E, \quad \%E = 100(1-q^n)\]

For \(n\) extractions, the amount of solute in each phase can be determined by:

- **Organic phase**: \(pq^{n-1}C_0V_2\)
- **Aqueous phase**: \(q^nC_0V_2\)

Solute concentrations can be found by:

- **Organic**: \(pq^{n-1}C_0V_2 / V_1 = pq^{n-1}C_0 / V_R\)
- **Aqueous**: \(q^nC_0V_2 / V_2 = q^nC_0\)

In our earlier example, 75% of a solute was removed with one extraction. We can determine how much would be removed from 10 sequential extractions.

\[n = 10\]
\[q = 0.25\]
\[E = 1 - 0.25^{10} = 1 - 9.6 \times 10^{-7}\]
\[\%E = 99.9999\%\]

A precursor to chromatography.

Multiple extractions can effectively remove a single species or a group of related species at the same time.

What do you do if the goal is to separate two or more species with similar \(D_c\) values?

Even if the \(D_c\) values for two species differ by 1000, you still can’t get better than 97% purity.

We can conduct a sequence of extractions to effect quantitative separation of multiple solutes - countercurrent extraction.

We transfer the extracting phase to the next tube and add fresh phase to the first.
Countercurrent extraction

\[ D_c = 1.0 \]

\[ V_m = V_s \]

Extraction # 1

\[ \text{Tubes} \]

\[ n = 0 \quad 1 \quad 2 \quad 3 \]

Totals

<table>
<thead>
<tr>
<th>A</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>100</td>
</tr>
</tbody>
</table>

First extraction

Next, the organic phase is transferred to the second tube. A new equilibrium is established.

\[ n = 0 \quad 1 \quad 2 \quad 3 \]

<table>
<thead>
<tr>
<th>Totals</th>
<th>3 B</th>
<th>97 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.91</td>
<td>2.91</td>
</tr>
<tr>
<td>B</td>
<td>0.09</td>
<td>94.09</td>
</tr>
</tbody>
</table>

Second extraction

\[ \text{Tots} \]

<table>
<thead>
<tr>
<th>A</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3</td>
</tr>
</tbody>
</table>

As the number of tubes are increased, the distribution of solutes appears more Gaussian. Ultimately, you can resolve them.

\[ n=6 \quad n=25 \quad n=100 \]

The peaks also become broader and shorter - they are distributed over a larger range of tubes.

Movement of solutes

Materials with larger \( D_c \) values tend to move along with the organic (mobile) phase more rapidly.

\[ \text{Fraction} \]

\[ \text{After 6 extractions} \]

Peak shape

As the number of tubes are increased, the distribution of solutes appears more Gaussian. Ultimately, you can resolve them.

\[ n=6 \quad n=25 \quad n=100 \]

The peaks also become broader and shorter - they are distributed over a larger range of tubes.
In some cases, it is difficult to efficiently remove a solute unless a large number of extractions are conducted.

An alternate approach is a continuous extraction.

With an appropriate setup, an efficient extraction can be conducted with a minimum of extracting solvent.

**Advantages**
- Only uses a small amount of solvent
- Can remove a high percent of a solute
- Can work unattended for long periods

**Setup**
- Dependent on relative density of liquids or if solids are to be extracted.

Setup when the extracting fluid is more dense.

Setup when the extracting solvent is less dense.

**For these systems to work**
- Density difference must be high
- Solute being collected must be less volatile than the extracting solvent
- Solute being collected must be thermally stable under conditions used.

Extraction times follow first order kinetics and are ranked based on half-life.

\[
\log t = \frac{-t_{1/2}}{\% E}
\]
Continuous extraction can also be applied to solids. Major limitation is a loss in efficiency during extraction due to channels developing in the solid.

An alternate approach to extracting solids. Repeated soaking of the solid prevents formation of channels. Rapid return of cool fluid can represent a hazard. Solvent should not be flammable.

- Some extraction methods
  - Organic species
    - “Like dissolves like”
  - Ionizing organic species
    - Limit ionization by controlling pH
  - Use of organic complexing reagents.
    - Many reagents available to complex metal ions - more soluble in organic phase.
  - Ion-association complexes
    - Formation of neutral ion pairs.

- Complexing reagents
  - Cupferron
    - Will form a complex with iron that can then be extracted.
    
    $3 \left( \begin{array}{c} \text{N} \\ \text{NO} \end{array} \right)^{-} \text{NH}_4^{+} \ + \ \text{Fe(III)}$

- Complexing reagents
  - Oxine - formation of an aluminum complex
    
    $3 \begin{array}{c} \text{N} \\ \text{O} \end{array}^{-} + \text{Al}^{3+}$

- Ion association complexes
  - At high levels of a complexing acid, it is possible to form a neutral species that is extractable.

    $\text{Fe(III)} \ + 6 \text{M HCl} \rightarrow \text{FeCl}_4^{-}$

    This can be extracted as HFeCl$_4$.

    To work: Conditions must favor formation of a large ion and the solvent must strongly solvate the ion pair.