Stationary Phases:

Stationary phase in GC is the main factor determining the selectivity and retention of solutes.

There are three types of stationary phases used in GC:
- Solid adsorbents
- Liquids coated on solid supports
- Bonded-phase supports

1.) Gas-solid chromatography (GSC)

- same material is used as both the stationary phase and support material
- common adsorbents include:
  - alumina
  - molecular sieves
  - silica
  - active carbon
  (crystalline aluminosilicates [zeolites])

Magnified Pores in activated carbon
2.) Gas-liquid chromatography (GLC)

- stationary phase is some liquid coated on a solid support
- over 400 liquid stationary phases available for GLC
  - many stationary phases are very similar in terms of their retention properties
- material range from polymers (polysiloxanes, polyesters, polyethylene glycols) to fluorocarbons, molten salts and liquid crystals

Based on polarity, of the 400 phases available only 6-12 are needed for most separations. The routinely recommended phases are listed below:

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical nature of polysiloxane</th>
<th>Max. temp.</th>
<th>McReynolds' constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>x' y' z'</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>μ' s'</td>
</tr>
<tr>
<td>SE-30</td>
<td>Dimethyl</td>
<td>350</td>
<td>14 53 44 64 41</td>
</tr>
<tr>
<td>Dexsil300</td>
<td>Carborane-dimethyl</td>
<td>450</td>
<td>43 64 111 151 101</td>
</tr>
<tr>
<td>OV-17</td>
<td>50% Phenyl methyl</td>
<td>375</td>
<td>119 158 162 243 202</td>
</tr>
<tr>
<td>OV-210</td>
<td>50% Trifluoropropyl</td>
<td>270</td>
<td>146 238 358 468 310</td>
</tr>
<tr>
<td>OV-225</td>
<td>25% Cyanopropyl-25% phenyl</td>
<td>250</td>
<td>238 369 338 492 386</td>
</tr>
<tr>
<td>Silar-SCP</td>
<td>50% Cyanopropyl-50% phenyl</td>
<td>275</td>
<td>319 495 446 637 531</td>
</tr>
<tr>
<td>SP-2340</td>
<td>75% Cyanopropyl</td>
<td>275</td>
<td>520 757 659 942 804</td>
</tr>
<tr>
<td>OV-275</td>
<td>Dicyanoallyl</td>
<td>250</td>
<td>629 872 763 1106 849</td>
</tr>
</tbody>
</table>

McReynolds' constants based on retention of 5 standard “probe” analytes
- Benzene, n-butanol, 2-pentanone, nitropropanone, pyridine

Higher the number the higher the absorption.

Preparing a stationary phase for GLC:
- slurry of the desired liquid phase and solvent is made with a solid support
  - solid support is usually diatomaceous earth (fossilized shells of ancient aquatic algae (diatoms), silica-based material)
- solvent is evaporated off, coating the liquid stationary phase on the support
- the resulting material is then packed into the column

disadvantage:
- liquid may slowly bleed off with time
  - especially if high temperatures are used
  - contribute to background
  - change characteristics of the column with time
3.) Bonded-Phase Gas chromatography
- covalently attach stationary phase to the solid support material
- avoids column bleeding in GLC
- bonded phases are prepared by reacting the desired phase with the surface of a silica-based support

  reactions form an Si-O-Si bond between the stationary phase and support
  or
  reactions form an Si-C-C-Si bond between the stationary phase and support

- many bonded phases exist, but most separations can be formed with the following commonly recommended bonded-phases:
  ① Dimethylpolysiloxane
  ② Methyl(phenyl)polysiloxane
  ③ Polyethylene glycol (Carbowax 20M)
  ④ Trifluoropropylpolysiloxane
  ⑤ Cyanopropylpolysiloxane

advantages:
- more stable than coated liquid phases
- can be placed on support with thinner and more uniform thickness than liquid phases

B. retention and capacity factor: \( t_R = t_M(1+k) \)

1. Modern methods: solute effects (Kamlet, Taft, and Abraham)

\[ \log k = c + rR_2 + s\pi_2 + a\Sigma\alpha_2 + b\Sigma\beta_2 + \log L \]

(Gas chromatography)

Solute descriptors \( (R_2, \pi_2, \Sigma\alpha_2, \Sigma\beta_2, \log L, \text{ and } V_x) \): depended on solute properties

Kamlet-Taft parameters

System constants \( (c, m, r, s, a, b, \text{ and } l) \): depended on chromatographic system conditions: mobile phase, stationary phase, and temperature.

2. Kovat’s Retention Index

\[ I = 100z + 100'[\log t_R^* (x)-\log t_R^* (z)]/[\log t_R^* (z+1)-\log t_R^* (z)] \]

Where \( t_R^* \) is the adjusted retention time, \( z \) the carbon number of the n-alkane eluting immediately before the substance of interest denoted by \( x \), and \( z+1 \) the retention number of the n-alkane eluting immediately after substance \( x \).
Retention Index  
(Kovats)  
Based on n-alkanes  

\[ I = 100 \left[ n + \frac{\log t'_N - \log t'_Nn}{\log t'_N(n+1) - \log t'_Nn} \right] \]  

where:  
\[ t'_N = \text{Net retention time} = t_r - t_0 \]  
and the analyte elutes between C_n and C_{n+1}  

Kovat’s approach is using retention of n-alkanes as standards to index the retention of substance of interest on a certain chromatographic system.
\[ I_{unk} = 100 \left[ 3 + \frac{\log(20.6 - 1.2) - \log(16.2 - 1.2)}{\log(25.0 - 1.2) - \log(16.2 - 1.2)} \right] \]

\[ I_{unk} = 356 \]

Retention Index (Kovats)

Based on the log-linear relationship between number of carbons (n) in an n-alkane and retention time.
3. McReynolds’ phase constants

\[ \Delta I = I_{\text{stationary phase}} - I_{\text{squalene}} \quad \text{Squalene (C}_{30}\text{H}_{62}) \]

McReynold's phase constants

\[ \Delta I = aX' + bY' + cZ' + dU' + eS' \]

Phase constant: 
- X’: Benzene; 
- Y’: 1-butanol; 
- Z’: 2-pentanone; 
- U’: 1-nitropropane; 
- S’: Pyridine

a, b, c, d, e, constants for the solute of interest.

Retention Index
(McReynolds Constant)

Reports \( \Delta I \) for a specific stationary phase (squalane), and 5 different reference compounds: benzene, n-butanol, 2-pentanone, nitropropane, pyridine

\[ \Delta I = I_{\text{sp}} - I_{\text{squalane}}. \]

From a table of stationary phase \( \Delta I \) values, one may choose the biggest \( \Delta I \) value for the reference compound most like the solute of interest.
McReynolds Constants: Example

- **Example:**
  - Kovats index of toluene:
    - 773 on SP squalene (non-polar)
    - 860 on SP dioctylphthalate
  - Define McReynolds constant as:
    - $\Delta l = 860 - 773 = 87$
  - Results:
    - Dioctylphthalate is a more polar stationary phase
    - The larger the McReynolds constant, the greater the retention time than compared to the non-polar column.

Method by McReynolds

$$\Delta l = aX' + bY' + cZ' + dU' + eS'$$

Phase constant: $X'$: Benzene; $Y'$: 1-butanol; $Z'$: 2-pentanone; $U'$: 1-nitropropane; $S'$: Pyridine

$a, b, c, d, e$, constants for the solute of interest.

Method by Kamlet, Taft, and Abraham

$$\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2 + l\log L$$  (Gas chromatography)

Solute descriptors ($R_2, \pi_2, \Sigma\alpha_2, \Sigma\beta_2, \log L^16$, and $V_a$): depended on solute properties

Kamlet-Taft parameters

System constants ($c, m, r, s, a, b$, and $l$): depended on chromatographic system conditions: mobile phase, stationary phase, and temperature.
Comparison to the method by Kamlet, Taft, and Abraham

Table 2.15
Proprietary solutes used by McReynolds (Rorschneider solutes in parentheses) to characterize stationary phase properties
$R_y = \text{excess refraction, } \gamma_a = \text{dipolarity/polarizability, } \Sigma a_j^D = \text{hydrogen-bond acidity, } \Sigma b_j^L = \text{hydrogen-bond basicity and } \log L_\text{16} = \text{partition coefficient at 25°C}.$

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Solvent</th>
<th>Solute descriptors</th>
<th>$R_y$</th>
<th>$\gamma_a$</th>
<th>$\Sigma a_j^D$</th>
<th>$\Sigma b_j^L$</th>
<th>$\log L_\text{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S'$</td>
<td>Pyridine</td>
<td>0.631</td>
<td>0.84</td>
<td>0</td>
<td>0.22</td>
<td>3.022</td>
<td></td>
</tr>
<tr>
<td>$H'$</td>
<td>2-Methyl-2-pentanol</td>
<td>0.180</td>
<td>0.50</td>
<td>0.51</td>
<td>3.628</td>
<td>1.963</td>
<td></td>
</tr>
<tr>
<td>$S'$</td>
<td>2-Octyne</td>
<td>0.233</td>
<td>0.30</td>
<td>0</td>
<td>0.10</td>
<td>3.850</td>
<td></td>
</tr>
<tr>
<td>$L'$</td>
<td>Dioxane</td>
<td>0.329</td>
<td>0.75</td>
<td>0.64</td>
<td>2.892</td>
<td>4.635</td>
<td></td>
</tr>
<tr>
<td>$M'$</td>
<td>cis-Hexadecane</td>
<td>0.436</td>
<td>0.25</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Idea is same: use constants from systems and solute to describe retention

Difference: Kamlet et al use solvatochromic parameters to index the constant of solute of interest.
McReynolds uses properties of specific molecules to index constant of solute of interest.
Standard model

- Log SP = c + eE + sS + aA + bB + IL
- Where
  - SP = solute property
  - L = gas-hexadecane partition coefficient
    - Cavity formation and solute-solvent dispersion interactions
  - E = excess molar refraction descriptor
  - A, B = hydrogen bonding acidity and basicity descriptors
Table 1
System constants for the poly(methyloctylsiloxane) stationary phase SPB-Octyl as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>System constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>e</td>
</tr>
<tr>
<td>60</td>
<td>0.092</td>
</tr>
<tr>
<td>80</td>
<td>0.118</td>
</tr>
<tr>
<td>100</td>
<td>0.135</td>
</tr>
<tr>
<td>120</td>
<td>0.154</td>
</tr>
<tr>
<td>140</td>
<td>0.168</td>
</tr>
<tr>
<td>160</td>
<td>0.176</td>
</tr>
<tr>
<td>180</td>
<td>0.185</td>
</tr>
<tr>
<td>200</td>
<td>0.190</td>
</tr>
<tr>
<td>220</td>
<td>0.190</td>
</tr>
<tr>
<td>240</td>
<td>0.198</td>
</tr>
<tr>
<td>260</td>
<td>0.200</td>
</tr>
</tbody>
</table>

Review
Separation methods for estimating octanol–water partition coefficients
Salwa K. Poole a,*, Colin F. Poole b

Abstract
Separation methods for the indirect estimation of the octanol–water partition coefficient (log P) are reviewed with an emphasis on high throughput methods with wide application range. The solubility parameter model is used to identify suitable separation systems for estimating log P in an efficient manner that requires the need for empirical trial and error experiments. With a few exceptions, systems based on reversed-phase chromatography employing chemically bonded phases are shown to be unsuitable for estimating log P for compounds of diverse structure. This is because the fundamental properties responsible for chromatographic retention tend to be different to those responsible for partition between octanol and water, especially the contribution from hydrogen bonding interactions. On the other hand, retention in several micellar and microemulsion liquid chromatography systems is shown to be highly correlated with the octanol-water partition coefficient. These systems are suitable for the rapid, high throughput determination of log P for neutral, weakly acidic, and weakly basic compounds. For compounds with a permanent charge, electrophoretic migration and electrospray interactions are fundamental to the stationary phase results in accurate estimation of partition coefficients. The experimental determination of solute descriptors offers an alternative approach for estimating log P, and other disassociation properties. A distinct advantage of this approach is that once the solute descriptors are known, solute properties can be estimated for any distribution or transport system for which a solution parameter model has been established.

Keywords: Reviews, Octanol–water partition coefficient
The determination of air/water partition coefficients for alkyl carboxylic acids by a new indirect method

Michael H. Abraham
Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H OAJ. E-mail: m.h.abraham@ucl.ac.uk

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The air-water partition coefficients of carboxylic acids, \( K_a \), especially those of high molecular weight, are very difficult to determine directly. Values of \( K_a \) can be obtained by an indirect method as \( K_a = K P \) where \( K \) is an air-solvent partition coefficient and \( P \) is the corresponding water-solvent partition coefficient. In the present method, gas-liquid chromatographic data and water-solvent partition data are used to obtain 'descriptors' of carboxylic acids that can then be used to determine the required \( K \) and \( P \), and thus \( K_a \) values. These are reported for all the 24 n-alkyl carboxylic acids from formic acid to n-tetraacetic acid, and for seven branched chain alkyl carboxylic acids. There is good agreement with literature values of \( K_a \), where available, although the present data on the n-alkyl carboxylic acids is much more self consistent than the literature data.

![Diagram of the indirect method]

**Table 2** Coefficients in eqn (3) for water-solvent partitions, as log \( P \), at 298 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( c )</th>
<th>( e )</th>
<th>( z )</th>
<th>( a )</th>
<th>( b )</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octan-1-ol</td>
<td>0.088</td>
<td>0.362</td>
<td>+1.054</td>
<td>0.034</td>
<td>3.460</td>
<td>3.814</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>0.249</td>
<td>0.480</td>
<td>-0.639</td>
<td>0.050</td>
<td>-2.284</td>
<td>2.708</td>
</tr>
<tr>
<td>Pentan-1-ol</td>
<td>0.175</td>
<td>0.375</td>
<td>-0.707</td>
<td>0.020</td>
<td>-3.337</td>
<td>3.249</td>
</tr>
<tr>
<td>Hexan-1-ol</td>
<td>0.143</td>
<td>0.718</td>
<td>-0.980</td>
<td>0.345</td>
<td>-3.314</td>
<td>3.403</td>
</tr>
<tr>
<td>Decan-1-ol</td>
<td>0.008</td>
<td>0.485</td>
<td>-0.934</td>
<td>0.015</td>
<td>-3.796</td>
<td>3.945</td>
</tr>
<tr>
<td>Oleyl alcohol</td>
<td>-0.339</td>
<td>-0.270</td>
<td>-0.525</td>
<td>0.055</td>
<td>4.042</td>
<td>4.204</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>0.314</td>
<td>0.001</td>
<td>0.022</td>
<td>-3.228</td>
<td>-4.337</td>
<td>4.239</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>0.327</td>
<td>0.157</td>
<td>-0.941</td>
<td>-3.191</td>
<td>4.343</td>
<td>4.191</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>0.268</td>
<td>0.173</td>
<td>-1.254</td>
<td>-3.556</td>
<td>4.308</td>
<td>4.589</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>0.227</td>
<td>0.278</td>
<td>-0.167</td>
<td>-2.816</td>
<td>4.324</td>
<td>4.205</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.361</td>
<td>0.570</td>
<td>-1.223</td>
<td>-3.399</td>
<td>-4.764</td>
<td>4.344</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.325</td>
<td>0.670</td>
<td>-2.061</td>
<td>-5.317</td>
<td>-4.733</td>
<td>4.543</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>0.087</td>
<td>0.667</td>
<td>-1.817</td>
<td>-5.387</td>
<td>-4.869</td>
<td>4.433</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.288</td>
<td>0.382</td>
<td>-1.686</td>
<td>-3.639</td>
<td>-3.000</td>
<td>4.561</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.139</td>
<td>0.784</td>
<td>-1.878</td>
<td>-3.740</td>
<td>-4.929</td>
<td>4.577</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.142</td>
<td>0.464</td>
<td>-0.338</td>
<td>-3.099</td>
<td>-4.625</td>
<td>4.491</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.143</td>
<td>0.327</td>
<td>-0.720</td>
<td>-3.610</td>
<td>-4.424</td>
<td>4.545</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.181</td>
<td>0.376</td>
<td>-0.603</td>
<td>-2.356</td>
<td>-4.420</td>
<td>4.265</td>
</tr>
<tr>
<td>Dodecane</td>
<td>0.248</td>
<td>0.561</td>
<td>-1.016</td>
<td>-2.226</td>
<td>-4.55</td>
<td>4.073</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.476</td>
<td>0.434</td>
<td>-0.939</td>
<td>-0.555</td>
<td>-5.185</td>
<td>4.189</td>
</tr>
<tr>
<td>Di-isopropyl ether</td>
<td>0.252</td>
<td>0.677</td>
<td>-1.506</td>
<td>-0.897</td>
<td>-5.549</td>
<td>4.815</td>
</tr>
<tr>
<td>Olive oil</td>
<td>0.001</td>
<td>0.577</td>
<td>-0.800</td>
<td>-1.470</td>
<td>-4.921</td>
<td>4.473</td>
</tr>
<tr>
<td>Tributylphosphate</td>
<td>0.015</td>
<td>0.804</td>
<td>-0.862</td>
<td>1.389</td>
<td>4.647</td>
<td>4.129</td>
</tr>
<tr>
<td>Gas phase</td>
<td>-0.994</td>
<td>0.577</td>
<td>2.549</td>
<td>3.813</td>
<td>4.041</td>
<td>-0.689</td>
</tr>
</tbody>
</table>
• Last lecture

Retention Index
(Rohrschnieder Constant)

Reports $\Delta I$ for different test solutes

$$\Delta I = I_{sp} - I_{\text{non-polar s.p.}}$$

From a table of $\Delta I$ values, one may choose the best stationary phase (s.p.) for a given class of solutes
Rules for Retention Index

1. R.I. increases 100 points for every CH₂ group in a molecule
2. ΔI for 2 isomers can be calculated from boiling points: ΔI ≈ 5 Δbp
3. R.I. for non-polar compounds is constant for any stationary phase.
4. R.I. for ANY compound is constant for ALL non-polar stationary phases.
5. ΔI for a solute between a polar and a non-polar stationary phase is a characteristic of the solute and can be predicted.

Kovats Retention Indices of Selected Hydrocarbons through C₁₀ on Bonded Phase Fused Silica Capillaries

A. J. Lubeck and D. L. Button
Marathon Oil Company, Denver Research Center, P. O. Box 260, Littleton, Colorado 80160, USA

Description of fused silica columns tested.

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>Film thickness [μm]</th>
<th>Column ID [mm]</th>
<th>Column length [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>J &amp; W</td>
<td>DB-1</td>
<td>0.25</td>
<td>0.264</td>
<td>60</td>
</tr>
<tr>
<td>H-P</td>
<td>PONA</td>
<td>0.5</td>
<td>0.21</td>
<td>50</td>
</tr>
<tr>
<td>J &amp; W</td>
<td>DB-1</td>
<td>1.0</td>
<td>0.259</td>
<td>60</td>
</tr>
<tr>
<td>J &amp; W</td>
<td>DB-5</td>
<td>0.25</td>
<td>0.252</td>
<td>60</td>
</tr>
<tr>
<td>J &amp; W</td>
<td>DB-5</td>
<td>1.0</td>
<td>0.259</td>
<td>60</td>
</tr>
</tbody>
</table>

DB-5 slightly more polar than DB-1
C thickness > A  E thickness > D