…back to resolution

$\alpha = \frac{K_B}{K_A}$ = selectivity factor!

$k' = \text{capacity factor} = \frac{(t_r - t_m)}{t_m}$

$R_s = \frac{t'_A - t'_B}{w_{avg}}$

$R_s = \frac{t_A^R - t_B^R}{t_B^R} \cdot \frac{\sqrt{N}}{4}$

$R_s = \frac{k'_B - k'_A}{1 + k'_B} \cdot \frac{\sqrt{N}}{4}$

$R_s = \frac{\sqrt{N} \left( \frac{\alpha - 1}{\alpha} \right) k'_B}{4 \left( 1 + k'_B \right)}$

**Figure 26-11** Separations at three resolutions. Here, $R_s = 2\Delta Z(W_A + W_B)$.

Here’s the selectivity term again
General Elution Problem: Resolution vs. Elution Time

(a) very slow elution
- last peaks are pretty broad
- all peaks base-line resolved

(b) fast separation
- all peaks are narrow
- 1,2 are not resolved

(c) the final compromise
- 1,2 barely resolved
- band widths are decent
  (for quantitative analysis)

Figure 26-14 Illustration of the general elution problem in chromatography.
Gas Chromatography

- Mobile Phase: Gas
  - He, N₂ most common
- Stationary phase: Solid-Liquid
  - packed column--particles (GS) or liquid/polymer coated particles (GL)
  - glass column wall or, hydrocarbon solvent covalently bound to wall
- Applications:
  - small organic molecules (MW < 10³)
  - research labs (industry, academia)
  - quality control, on-line process control
  - environmental
Like dissolves Like

- Chemical Principle: ionic or very polar solids are more soluble in polar (ionic) solvents (alcohols, acetone, acetonitrile)
- Weakly polar, nonpolar compounds are only soluble in apolar solvents (toluene, ether, hexane)

[Chemical structures for Acetone and Hexane]
Getting the Sample

- Volatile gases can be collected in a gas tight glass syringe
- Small needle is inserted through a rubber septum (same septum is on the GC)
- Or (commonly) volatile liquids are injected
- Solvent, (like acetone, acetonitrile) must not co-elute with any analyte of interest
Precise flow monitoring required, $\mu$

Automation possible here with sophisticated valves

"inert" carrier gas, e.g., He, N$_2$

Temperature control very important for optimized separations

Figure 27-1  Schematic of a gas chromatograph.
Get the sample loaded

• Injection port designed to limit unwanted vapor from entering column
• typically 1-10 µL syringe used
• splitter diverts appr. 99% of the sample away from column
  – required by some very small capillaries
• chamber preheated to >50 °C of the least volatile analyte carrier gas stream moves analyte onto the capillary

![Figure 27-3](image-url) Cross-sectional view of a microflash vaporizer direct injector.
Temperature Programming

$K_{\text{part}}$ in GC--depends on solute/stationary phase and temperature

Increase temperature during a separation--decreases $K$
  a.k.a. temperature gradient, temperature ramp

typically $2^\circ$-$10^\circ$/minute, today even faster
ovens are very stable and uniform

Premise: vapor pressure strongly dependent on temperature

$$\ln p = \frac{\Delta v H}{RT} + \text{const}$$  
Clausius-Clapeyron equation  
$\Delta v H$. Partial molar enthalpy of vaporization

partitioning of give solute between gas and solid/liquid phase
depends on energy of interaction (solvation, adsorption) and
its vapor pressure! Temperature changes cause change in p
Separations at Various Temperatures

Recall the “general elution problem”
• either poor separations or really long experiment times

Demonstrates the improved performance of a linear temperature ramp.
note, better selectivity, better peak widths. (both used to calculate resolution)
Stationary Phases--example

Normal surface of quartz column (hydrophobic)

1) functionalize with dimethylchlorosilane

\[ \text{Si-OH} + \text{Cl-Si-Cl} \rightarrow \text{Si-O-Si-Cl + HCl} \]

Variations:
- phenyl instead of methyl
- more non-polar
- propyl or trifluoropropyl
- at step 2) use glycol
  - polyethylene glycol
  - great for alcohols, acids

2) add an alcohol

3) add more DMCS (repeat)

- results in polydimethylsiloxane film

the all-purpose GC column
<table>
<thead>
<tr>
<th>Stationary Phase</th>
<th>Common Trade Name</th>
<th>Maximum Temperature, °C</th>
<th>Common Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydimethyl siloxane</td>
<td>OV-1, SE-30</td>
<td>350</td>
<td>General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs</td>
</tr>
<tr>
<td>Poly(phenylmethylidimethyl) siloxane (10% phenyl)</td>
<td>OV-3, SE-52</td>
<td>350</td>
<td>Fatty acid methyl esters; alkaloids; drugs; halogenated compounds</td>
</tr>
<tr>
<td>Poly(phenylmethyl) siloxane (50% phenyl)</td>
<td>OV-17</td>
<td>250</td>
<td>Drugs; steroids; pesticides; glycols</td>
</tr>
<tr>
<td>Poly(trifluoropropylidimethyl) siloxane</td>
<td>OV-210</td>
<td>200</td>
<td>Chlorinated aromatics; nitroaromatics; alkyl-substituted benzenes</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>Carbowax 20M</td>
<td>250</td>
<td>Free acids; alcohols; ethers; essential oils; glycols</td>
</tr>
<tr>
<td>Poly(dicyanoallyldimethyl) siloxane</td>
<td>OV-275</td>
<td>240</td>
<td>Polyunsaturated fatty acids; rosin acids; free acids; alcohols</td>
</tr>
</tbody>
</table>
Elution not simply based on bp values!!!
poly(dimethyl)siloxane phase

Detector response

Time (min)

(a) Nonpolar stationary phase
Example Application

- Kovats’ Retention Indices
- Qualitative Analysis
- based on adjusted retention time, $t_s'$
- derived for normal alkane series
- extrapolate values for highly branched or unsaturated compounds

**Figure 27-12** Graphical illustration of the method for determining retention indexes for three compounds. Stationary phase: squalane. Temperature: 60°C.
Thermal Conductivity Detector

- Sensitive to both hydrocarbons and inorganic species
- Temperature response of a wire filament as column flow passes by
- Carrier gas is either H₂ or He
  - 5-6 times the thermal conductivity of most other analytes
- Inexpensive; non-destructive

Detection limit .3 ng/ml (slower response)
Linear response $10^4$

Resistance of element in carrier gas compared to column eluent stream

Temp of wire changes---as organic species elute--this changes resistance of wire!
Flame Ionization Detector

- Detection limit 4 pg/s
- Linear over $10^7$

- The most common detector
- Good for most hydrocarbons
  - Oxygen, nitrogen, sulfur functional groups reduced response
- Analyte is burned in an oxygen/hydrogen flame
- Ions produced are detected as current on the collector electrode
- Rugged and easy to operate
- No background non-ionized species like water

\[ i \alpha nC \text{ (mass not concentration)} \]

\[ \text{except } C=O \text{ } C=N, \text{ } C≡N \]