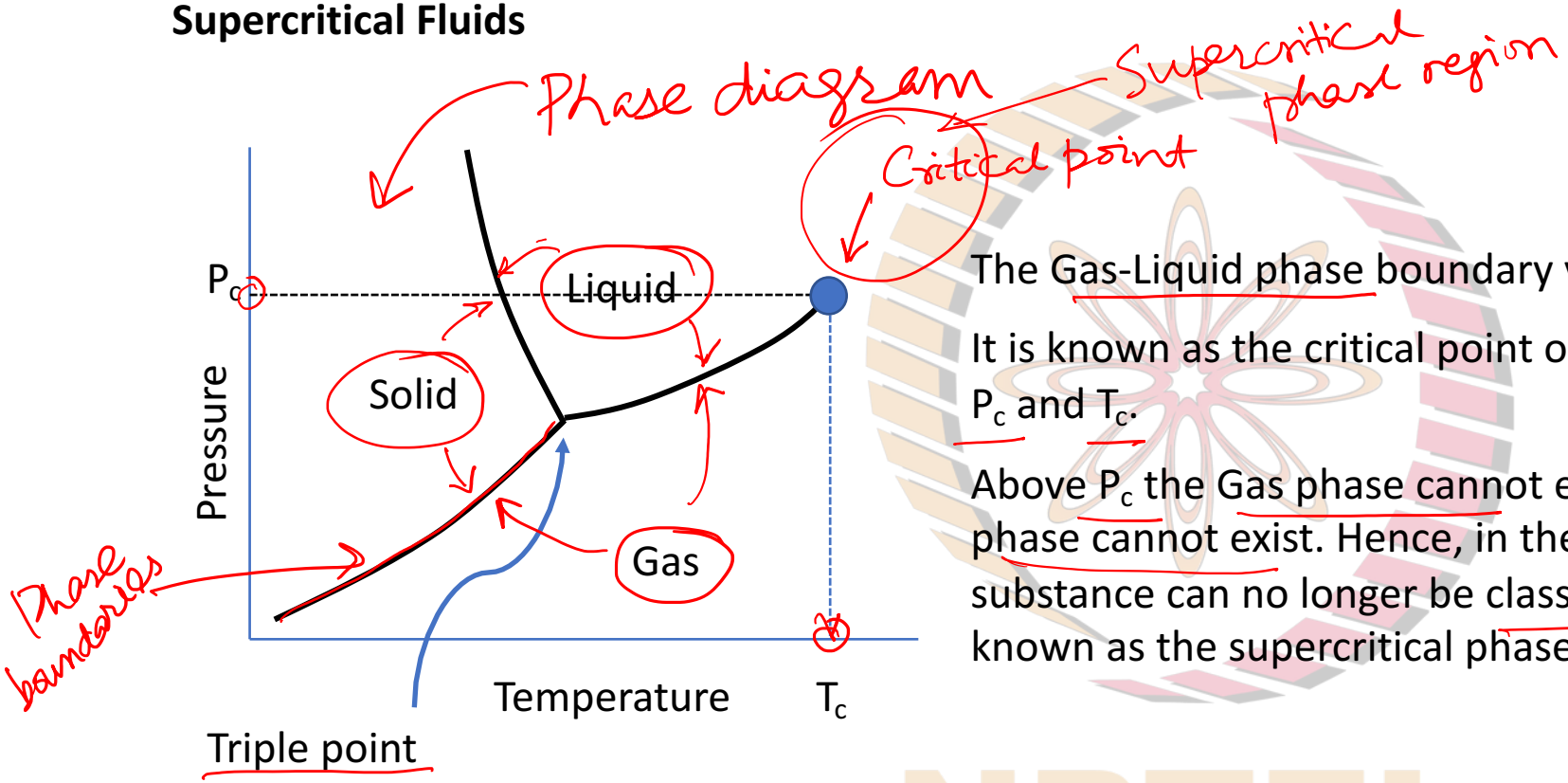
Quantitative Methods in Chemistry

Week 8, Lecture 3

This week: Practice of Chromatography – HPLC, Gas Chromatography, Supercritical Fluid Chromatography, Detectors for analytes

This lecture: Supercritical Fluid Chromatography (SFC)

Supercritical Fluids



The Gas-Liquid phase boundary vanishes beyond this point.

It is known as the critical point of a substance. It is defined by P_c and T_c.

Above P_c the Gas phase cannot exist and above T_c the liquid phase cannot exist. Hence, in the region $>P_c$ and $>T_c$, the substance can no longer be classified as liquid or gas. It is known as the supercritical phase.

All the three phases coexist in thermodynamic equilibrium

Examples of Common Supercritical Fluids

Solvent	T_c (℃)	P_c (Bar)
Carbon dioxide	31.1	73.8
Nitrous oxide	36.6	72.3
Ethane	32.2	48.9
$CClF_3$	28.8	39.5
Ethylene	9.3	50.4

Physical Properties of Supercritical Fluids

Property	Liquid	Gas	Supercritical Fluids
Density (g/cm^3)	~1.0	0.001	0.2 – 0.8
Viscosity (mPa · s)	0.5 – 1.0	0.01	0.05 – 0.1
Diffusivity range (cm^2/s)	10^{-5}	10^{-1}	~10^{-3}

Density similar to liquid phase

Viscosity similar to Gaseous phase

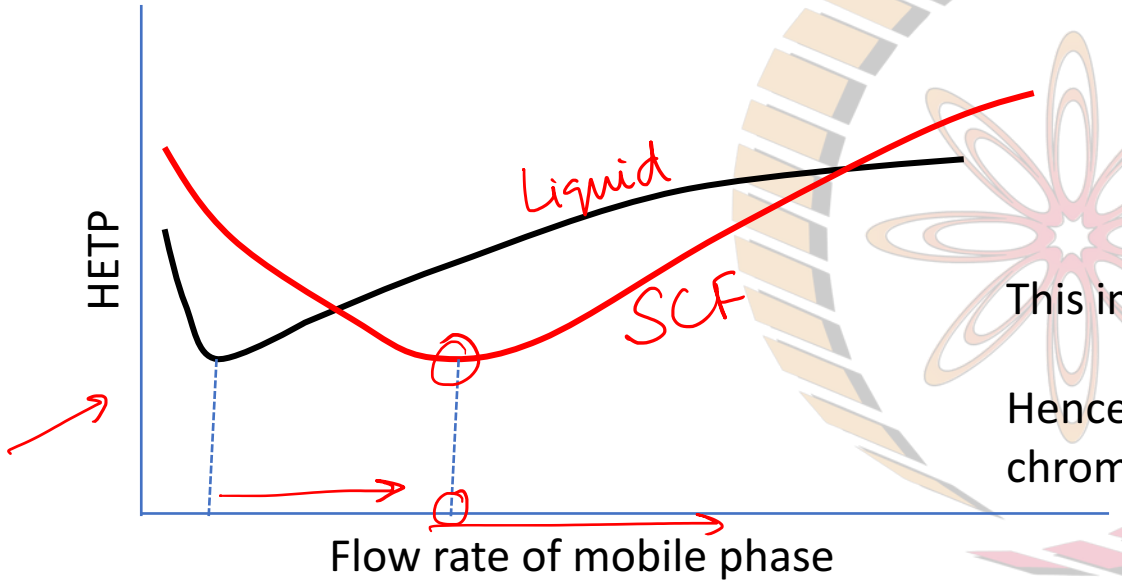
Intermediate diffusivity.

NOTE: All of these properties are strongly altered as temperature or pressure are changed!

Characteristics of Supercritical Fluids

- Can be considered as gases that have been compressed to liquid-like densities.
- They exhibit **high densities** like those of liquids – For chromatography, this means SCFs interact (solvate) the analyte much better than gas.
- They have **low viscosities** which are gas-like – For chromatography, this means lower back-pressure, lower pressure drop across the column
- Low viscosities of SCFs imply more efficient mass transfer processes and hence smaller resistance to mass transfer term (C_M) for SCFs. → More efficient separations
- Lower viscosities of SCFs imply that we can work at much **higher flow rates** in chromatographic separations.
- SCFs also have higher diffusivities than typical liquids – For chromatography this means SCFs can penetrate well into the pores and the voids existing in stationary phase, and hence, can elute out analytes out of them more efficiently. Smaller C_S term Van Deemter equation

SCFs can have much higher optimized flow rates



This implies much **faster separations** in SFC compared to LC.

Hence, we can have much **higher throughput** from the chromatography system.

Comparison between the chromatographic performances

Technique	LC	GC (open tubular)	SFC (open tubular)
Flow rates (cm/s)	0.1 – 0.4	1 – 5	0.5 – 4.0
Elution time (min)	2.5 – 10	6 – 20	15 – 50
Plate count (N)	3000 – 10,000	50,000 – 300,000	50,000 – 300,000
Plate Height (H, cm)	0.002	0.02	0.002
Column Length (L, m)	0.12	100	100

Advantages and Limitations of the SFC

Comparison with HPLC

- Better resolutions
- Less waste
- Higher throughput
- Limited choice of mobile phase
- Limited solubility of analyte in the mobile phase
- Unsuited for water-soluble analytes
- Unwanted reactions with the mobile phase

Comparisons with GC

- Better solvation of analytes
- Greater range of samples
- Suitable for temperature sensitive analytes
- Organic Modifiers can be added to alter the polarity of the mobile phase
- Hardware complexity
- Limited choice of mobile phase
- Unwanted reactions
- Adding organic additives may prevent the use of certain detectors

Use of Organic Modifiers

Supercritical CO_2 is the most commonly used SCF. However, it is quite non-polar and not efficient for eluting out polar analytes.
So, often, Organic solvents are mixed with SC-CO_2 to:

- Increase the polarity of the mobile phase
- Facilitate elution of polar analytes

The organic modifiers include **Methanol** and **Acetonitrile** which are both polar and miscible with CO_2.

SC-CO_2 in extraction processes: It is industrially used to decaffeinate coffee beans. The advantage of using SCFs is that they can be readily converted from a fluid phase to a gaseous phase by simple change of temperature or pressure. This allows rapid recovery of the solute from the SCFs.