

# EG3029 Chemical Thermodynamics

## Volumetric Properties of Pure Fluids

# $P V T$ Behaviour

## General

- Equations of state to describe relations of pressure, temperature and volume

- for example

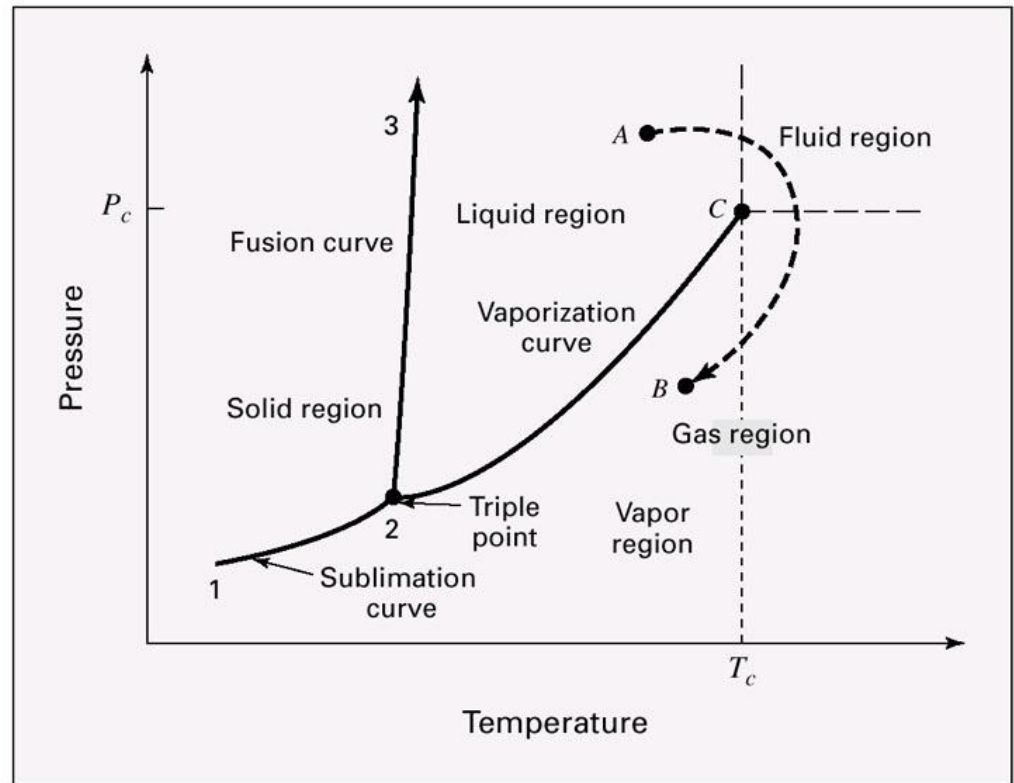
$$P V = R T$$

- important for industrial processes
  - parameters like  $P$ ,  $V$  and  $T$  can be measured
  - parameters like  $U$  and  $H$  can then be calculated
  - process can be described mathematically

# $P V T$ Behaviour

## $P T$ Diagram

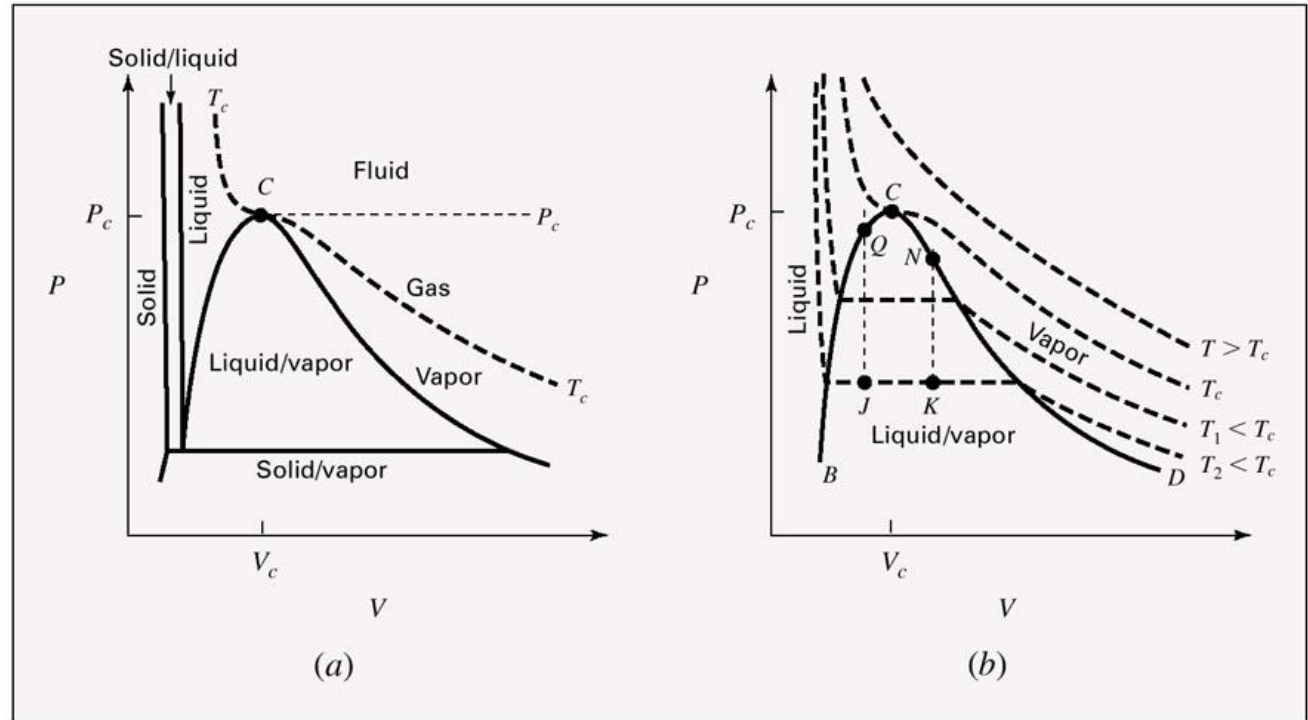
- Recall the Phase Rule
  - $F = 0$  at triple point (invariant)
  - $F = 1$  on two-phase lines (univariant)



- Disadvantage: no information about volume

# $P V T$ Behaviour

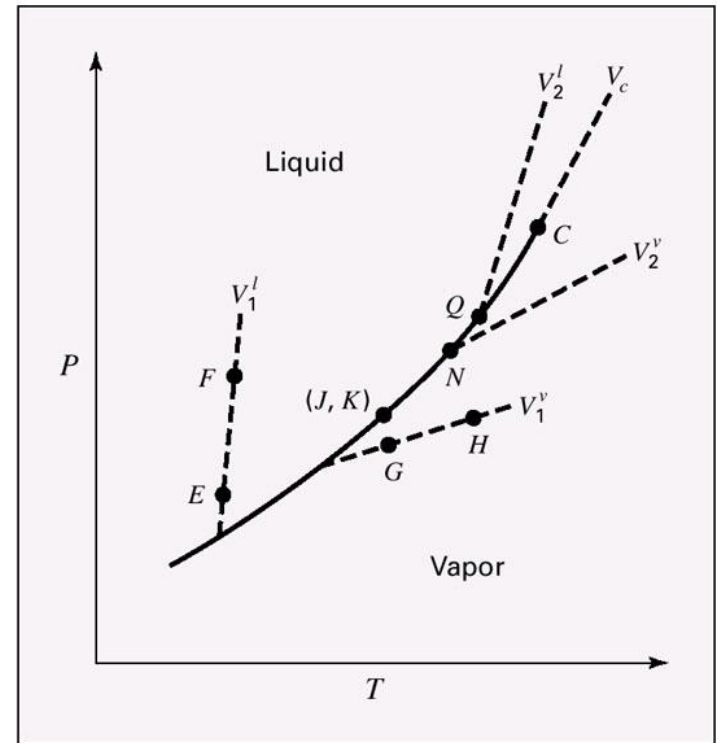
## $P V$ Diagram



# $P$ $V$ $T$ Behaviour

## Critical Point

- $C$  represents the end of the vaporization curve
- Highest  $P$  and  $T$  ( $P_C$ ,  $T_C$ ) at which a pure chemical can exist in VLE
- Supercritical fluids have great potential for practical applications



# $P V T$ Behaviour

## Single-Phase Regions

- General  $EOS$

$$f(P, V, T) = 0$$

delivers for the volume  $V = V(P, T)$

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$\frac{dV}{V} = \beta dT - \kappa dP$$

with

$$\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

*Volume expansivity*

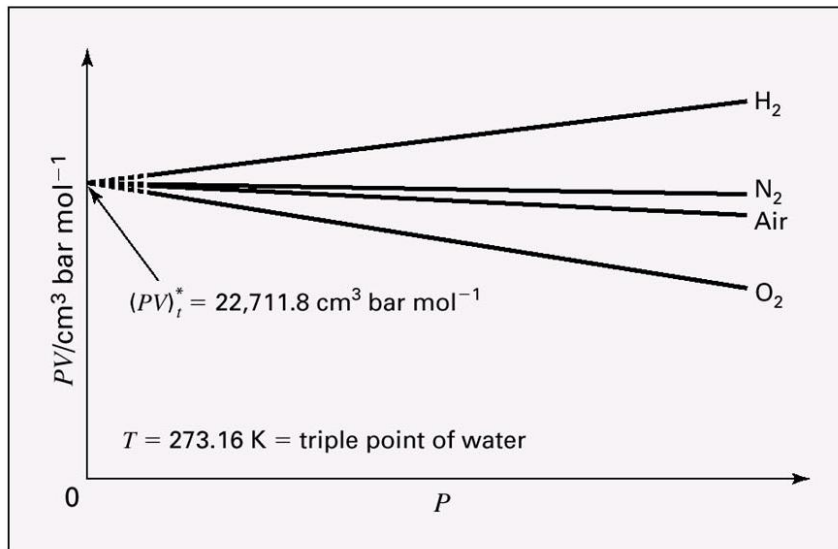
$$\kappa \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

*Isothermal compressibility*

# Virial Equations of State Ideal Gas

- Virial *EOS*

$$PV = a + bP + cP^2 + \dots = a(1 + B'P + C'P^2 + D'P^3 + \dots)$$



Compressibility factor

$$Z \equiv \frac{PV}{RT}$$

# EOS: Equations of State

## Virial Equations

- Low pressure case (may work up to several bars)

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

- Elevated pressure case (but subcritical)

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

- Benedict/Webb/Rubin equation

$$P = \frac{RT}{V} + \frac{B_0RT - A_0 - \frac{c_0}{T^2}}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2} \cdot \left(1 + \frac{\gamma}{V^2}\right) \cdot \exp\left(-\frac{\gamma}{V^2}\right)$$

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$  are constants for a given fluid



# EOS: Equations of State

## Cubic Equations

- Van der Waals EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

- Generic cubic EOS:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)}$$

$$a(T) = \psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}$$

$$b = \Omega \frac{RT_c}{P_c}$$

$\varepsilon, \sigma, \Psi, \Omega$  are pure numbers  
 $T_c, P_c$  are state functions at  
 critical point

- Redlich/Kwong EOS:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

$$\alpha(T_r) = \frac{1}{\sqrt{T_r}}$$

# EOS: Equations of State

## Cubic Equations

- Theorem of corresponding states:

$$T_r \equiv \frac{T}{T_c}$$

reduced temperature

$$P_r \equiv \frac{P}{P_c}$$

reduced pressure

***All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behaviour to about the same degree.***

- Acentric factor:

$$\omega \equiv -1.0 - \log(P_r^{sat})_{T_r=0.7}$$

$P_r^{sat}$  reduced vapour pressure

# EOS: Equations of State

## Cubic Equations

- Vapour & vapour-like roots:

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \varepsilon\beta)(Z + \sigma\beta)}$$

$$\beta = \Omega \frac{P_r}{T_r}$$

$$q = \frac{\Psi \alpha(T_r)}{\Omega T_r}$$

computationally solved by iterative procedures (start:  $Z = 1$ )

- Liquid & liquid-like roots:

$$Z = \beta + (Z + \varepsilon\beta)(Z + \sigma\beta) \left( \frac{1 + \beta - Z}{q\beta} \right)$$

# EOS: Equations of State

## Cubic Equations

- Parameter assignments

| Eq. of State | $\alpha(T_r)$                                | $\sigma$       | $\epsilon$     | $\Omega$ | $\Psi$  | $Z_c$   |
|--------------|--|----------------|----------------|----------|---------|---------|
| vdW (1873)   | 1  | 0              | 0              | 1/8      | 27/64   | 3/8     |
| RK (1949)    | $T_r^{-1/2}$                                 | 1              | 0              | 0.08664  | 0.42748 | 1/3     |
| SRK (1972)   | $\alpha_{\text{SRK}}(T_r; \omega)^{\dagger}$ | 1              | 0              | 0.08664  | 0.42748 | 1/3     |
| PR (1976)    | $\alpha_{\text{PR}}(T_r; \omega)^{\ddagger}$ | $1 + \sqrt{2}$ | $1 - \sqrt{2}$ | 0.07780  | 0.45724 | 0.30740 |

$$^{\dagger}\alpha_{\text{SRK}}(T_r; \omega) = \left[ 1 + (0.480 + 1.574 \omega - 0.176 \omega^2) (1 - T_r^{1/2}) \right]^2$$

$$^{\ddagger}\alpha_{\text{PR}}(T_r; \omega) = \left[ 1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2) (1 - T_r^{1/2}) \right]^2$$

vdW: van der Waals; RK: Redlich-Kwong; SRK: Soave-Redlich-Kwong; PR: Peng-Robinson

# Heat Effects

## General

- When heat is transferred to a system many phenomena can happen:
  - Temperature change
  - Phase transition
  - Chemical reaction
  - Composition change
- Temperature dependence of thermodynamic parameters and heat capacities

# Heat Effects

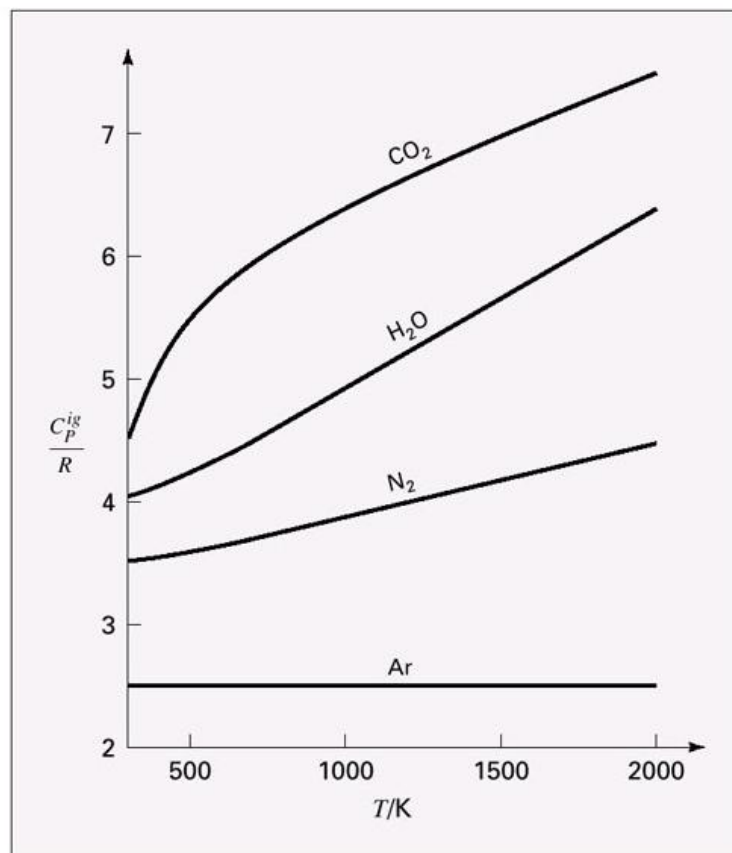
## Heat Capacities

- Change of internal energy and enthalpy
  - Typically empirical equations:

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2$$

$$\frac{C_P}{R} = a + bT + cT^{-2}$$

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$$



# Heat Effects Outlook

- Latent heat of phase changes

$$\Delta H = T \cdot \Delta V \cdot \frac{dP^{sat}}{dT}$$

- Standard heat of reaction

$$\Delta H = Q$$

- Standard heat of formation
  - Formation of a compound from its elements