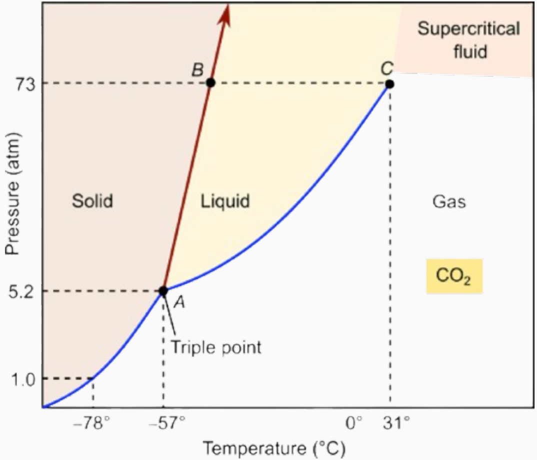
Lecture 11: Law of Corresponding States

Phase Diagram, Law of Corresponding States

Phase Diagrams - Gen Chem

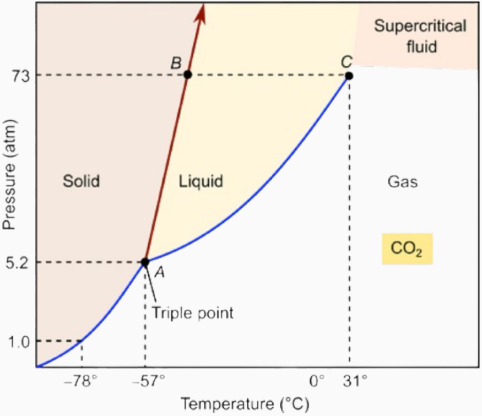


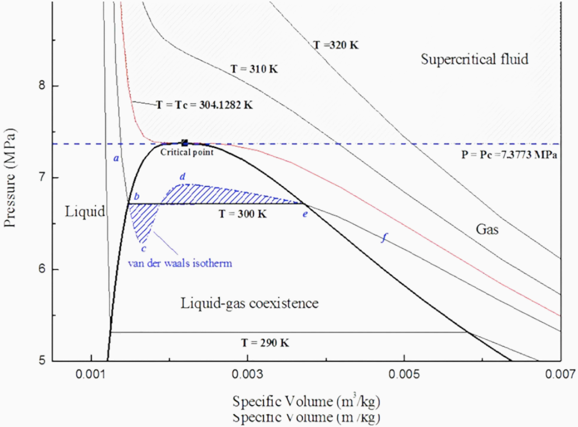
Critical Point (T_C): Point where liquid and gas phases are indistinguishable; temperature where gas cannot be liquidfied

Triple Point: Point where solid, liquid, and gas phases coexist

Critical Properties (P_C, $\overline{V_C}$): Pressure and molar volume of a substance at T_C

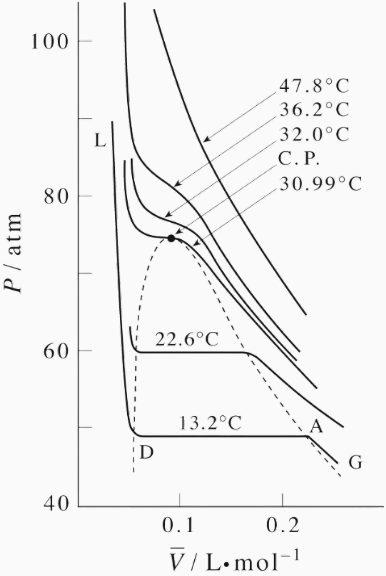
Phase Diagrams - PChem





Isotherm: constant temperature curve

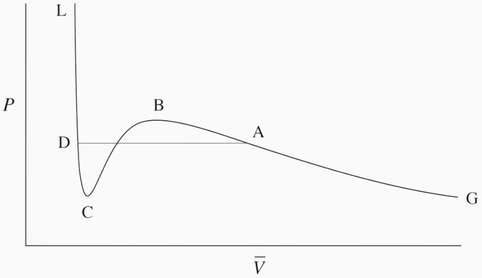
Phase Diagrams - Coexistance Region, Real Gas



Consider the path traced by $G \to A \to D \to L$

- Phase change from gas to liquid by increasing pressure
- $A \to D$: liquid–gas coexistance region
- Region decreases as temperature increases, until merge to T_C

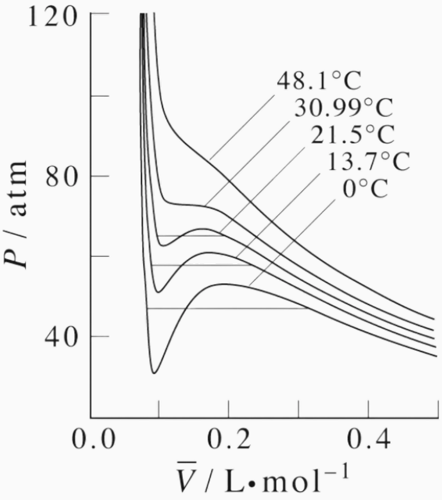
Phase Diagrams - Spurious Loops in VDW



Consider the path traced by $G \to A \to D \to L$

- VDW model has spurious loops $\frac{\partial P}{\partial \overline{V}} > 0$
- Solving cubic gives 3 roots, A, D, and unstable middle point

Phase Diagrams - Merging of Roots to determine T_C



(a)

Consider the critical point T_C

- Inflection point: $\left(\frac{\partial P}{\partial V}\right)_T = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$
- Point where 3 roots becomes one root is the critical point T_C

Van der Waals Critical Constants

Start from VDW cubic form:

$$\overline{V}^3 - \left(b + \frac{RT}{P}\right)\overline{V}^2 + \frac{a}{P}\overline{V} - \frac{ab}{P} = 0$$

At triple point, we have a triply degenerate root:

$$(\overline{V} - \overline{V}_c)^3 = 0 \quad \Rightarrow \quad \overline{V}^3 - 3\overline{V}_c\overline{V}^2 + 3\overline{V}_c^2\overline{V} - \overline{V}_c^3 = 0$$

Compare the coefficients:

$$b + \frac{RT_c}{P_c} = 3\overline{V}_c \qquad \frac{a}{P_c} = 3\overline{V}_c^2 \qquad \frac{ab}{P_c} = \overline{V}_c^3$$

Solve for $\overline{V}_c$, P_c, and T_c in terms of a, b:

$$\frac{ab}{P_c} = \overline{V}_c^3 \implies P_c = \frac{ab}{\overline{V}_c^3}$$

$$\frac{a}{P_c} = 3\overline{V}_c^2 \implies P_c = \frac{a}{3\overline{V}_c^2} \implies \frac{ab}{\overline{V}_c^3} = \frac{a}{3\overline{V}_c^2} \implies \boxed{\overline{V}_c = 3b}$$

Van der Waals Critical Constants

Substitute $\overline{V}_c = 3b$ in:

$$P_c = \frac{a}{3\overline{V}_c^2} \implies P_c = \frac{a}{3(3b)^2} = \boxed{\frac{a}{27b^2}}$$

From $b + \frac{RT_c}{P_c} = 3\overline{V}_c$:

$$b + \frac{RT_c}{P_c} = 9b \implies \frac{RT_c}{P_c} = 8b$$

$$T_c = \frac{8bP_c}{R} = \boxed{\frac{8a}{27bR}}$$

Van der Waals Critical Constants

$$\overline{V}_c = 3b \qquad P_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27bR}$$

Law of Corresponding States

Recognize that the Zs are constant

TABLE 16.5
The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\overline{V}_c$/L·mol^{-1}	$P_c\overline{V}_c/RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443
Water	647.126	220.55	217.66	0.05595	0.2295
Ammonia	405.30	111.30	109.84	0.07250	0.23945
Methane	190.53	45.980	45.379	0.09900	0.28735
Ethane	305.34	48.714	48.077	0.1480	0.28399
Ethene	282.35	50.422	49.763	0.1290	0.27707
Propane	369.85	42.477	41.922	0.2030	0.28041
Butane	425.16	37.960	37.464	0.2550	0.27383
2-Methylpropane	407.85	36.400	35.924	0.2630	0.28231
Pentane	469.69	33.643	33.203	0.3040	0.26189
Benzene	561.75	48.758	48.120	0.2560	0.26724

$$\overline{V}_c = 3b \qquad P_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27bR}$$

- van der Waal:

$$Z = \frac{P_c\overline{V}_c}{RT_c} = \frac{3}{8}$$

- Redlich-Kwong

$$Z = \frac{P_c\overline{V}_c}{RT_c} = \frac{1}{3}$$

- Peng-Robinson

$$Z = \frac{P_c\overline{V}_c}{RT_c} = 0.3074$$

van der Waals Law of Corresponding States

Law of Corresponding States

Properties of all gases are identical if we compare them under relative conditions to their critical point

Substitute vdw with rearranged vdw parameters:

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT \qquad a = 3P_c\overline{V}_c^2 \quad b = \frac{1}{3}\overline{V}_c$$

$$\left(P + \frac{3P_c\overline{V}_c^2}{\overline{V}^2}\right)\left(\overline{V} - \frac{1}{3}\overline{V}_c\right) = RT$$

Divide both sides by $P_c\overline{V}_c$:

$$\left(\frac{P}{P_c} + \frac{3\overline{V}_c^2}{\overline{V}^2}\right)\left(\frac{\overline{V}}{\overline{V}_c} - \frac{1}{3}\right) = \frac{RT}{P_c\overline{V}_c}$$

van der Waals Law of Corresponding States

Rearrange Critical Relation:

$$\frac{P_c\overline{V}_c}{RT_c} = \frac{3}{8} \implies \frac{RT}{P_c\overline{V}_c} = \frac{8}{3}\frac{T}{T_c}$$

Substitute:

$$\left(\frac{P}{P_c} + \frac{3\overline{V}_c^2}{\overline{V}^2}\right)\left(\frac{\overline{V}}{\overline{V}_c} - \frac{1}{3}\right) = \frac{8}{3}\frac{T}{T_c}$$

van der Waals Equation in Reduced Variables

This is a universal equation - no gas specific a or b variables

$$\left(P_r + \frac{3}{\overline{V_r}^2}\right)\left(\overline{V_r} - \frac{1}{3}\right) = \frac{8}{3}T_r$$

Where we defined reduced variables $P_r = \frac{P}{P_c}$ $\overline{V_r} = \frac{\overline{V}}{\overline{V}_c}$ $T_r = \frac{T}{T_c}$