Statistical Molecular Thermodynamics

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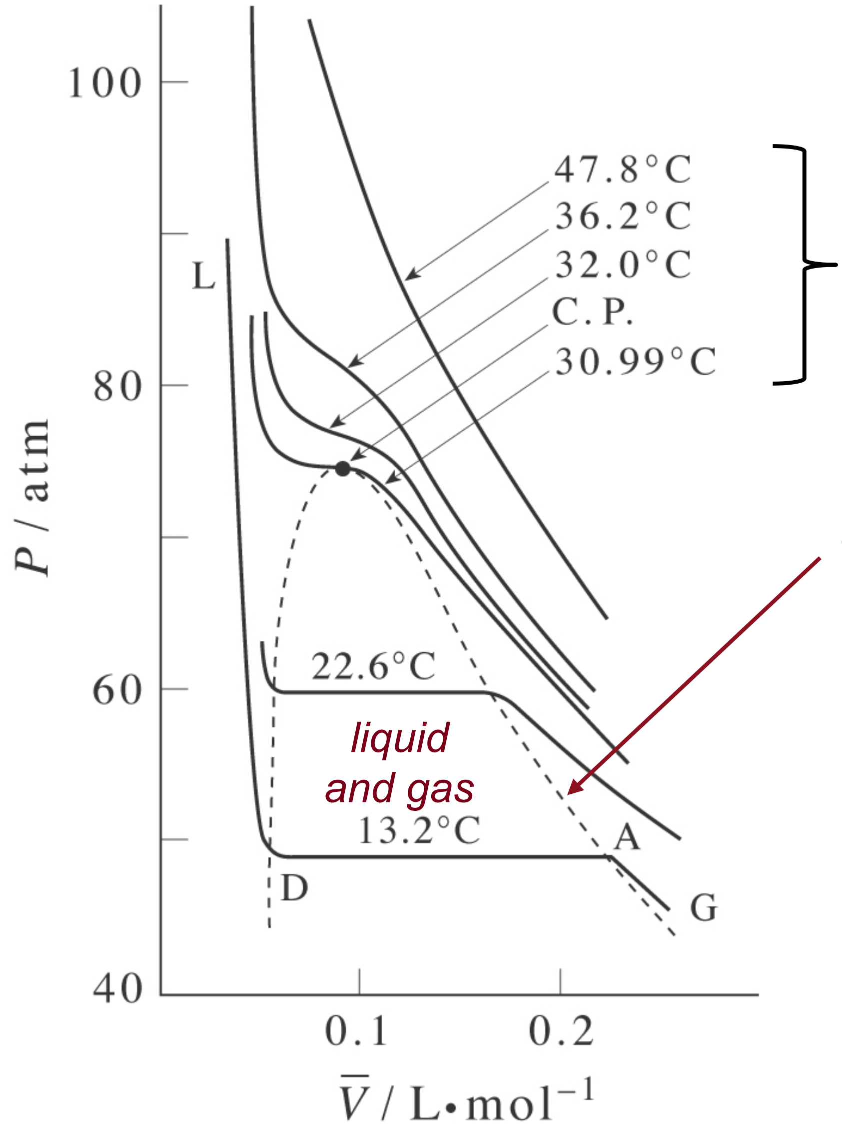
Video 2.3

Gas-Liquid *PV* Diagrams

PV Diagram for Carbon Dioxide



Isotherms
(plots of P vs $\overline{V}$ at constant T)

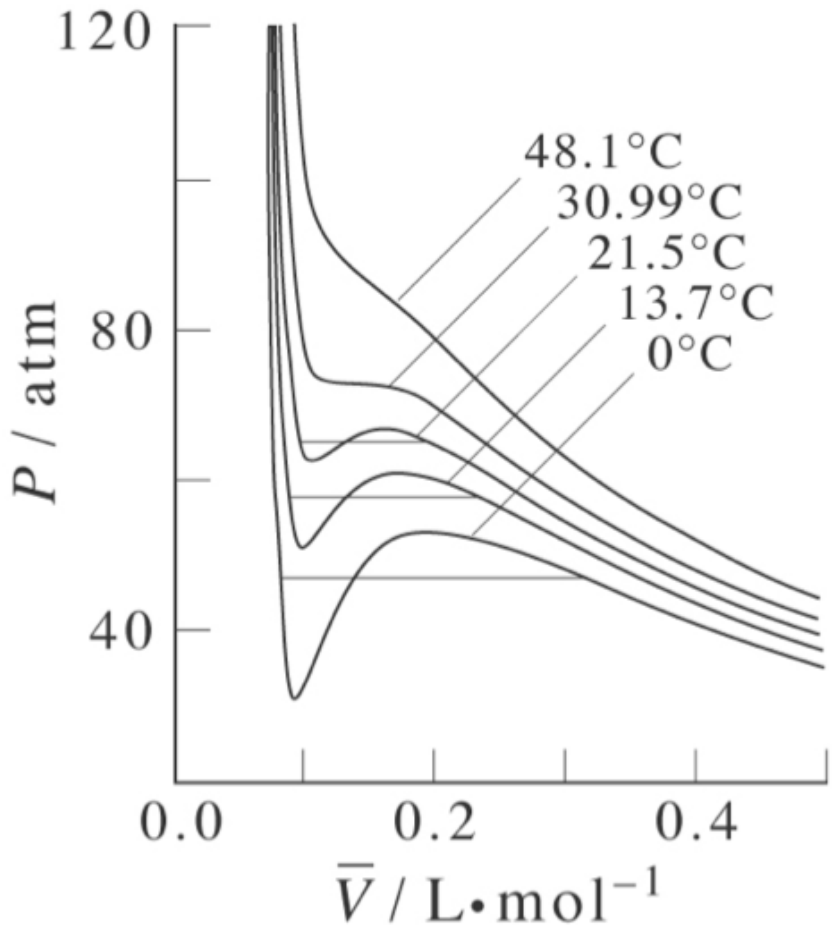
coexistence curve

The temperature above which a gas can not be liquefied is called the critical temperature (T_c)

As T approaches T_c, the curves flatten

At $T < T_c$ there are horizontal regions where gas and liquid co-exist

Non-ideal Cubic Equations of State



van der Waals EOS

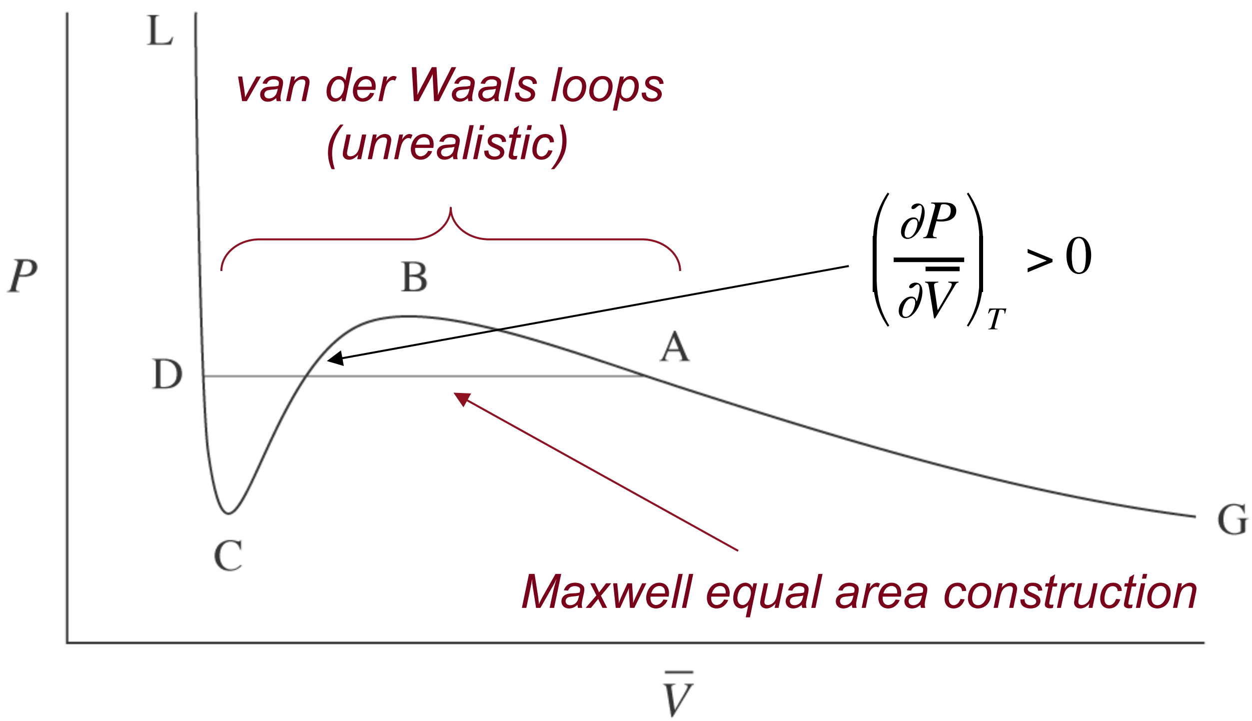
$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$$

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

Redlich-Kwong and Peng-Robinson are also cubic and show similar behavior

vdW Cubic Equation of State

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



As a cubic equation, there are 3 real roots for temperatures below T_c, which come closer and closer together and ultimately merge to a single, triply degenerate root at $T = T_c$, $P = P_c$, and $V = V_c$.

At that point:

$$\left(\overline{V} - \overline{V}_c\right)^3 = 0$$

$$\overline{V}^3 - 3\overline{V}_c\overline{V}^2 + 3\overline{V}_c^2\overline{V} - \overline{V}_c^3 = 0$$

Solution for the Critical Isotherm

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

Valid for $T = T_c$: $$\overline{V}^3 - 3\overline{V}_c\overline{V}^2 + 3\overline{V}_c^{\,2}\overline{V} - \overline{V}_c^3 = 0$$

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

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

…and that's how van der Waals equation of state parameters are determined! From best fitting to the critical point observables for individual gases.

Critical Compressibility

TABLE 2.5
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
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443

$$\frac{P_c\overline{V}_c}{RT_c} = \frac{1}{R}\left(\frac{a}{27b^2}\right)(3b)\left(\frac{27bR}{8a}\right) = 0.375!$$

there is an apparent correspondence *between different "real" gases that is entirely independent of the van der Waals equation of state*