

Gas-Liquid PV diagram

Law of Corresponding States

Source of Slides : Internet.
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Lecture 1

VDW Equation of State and Experiment

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

① Low pressure region
volume is large $V \gg b$

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

$$\Rightarrow \frac{PV}{RT} = 1 - \frac{a}{V \times RT}$$

$$\Rightarrow Z = 1 - \frac{a}{VRT}$$

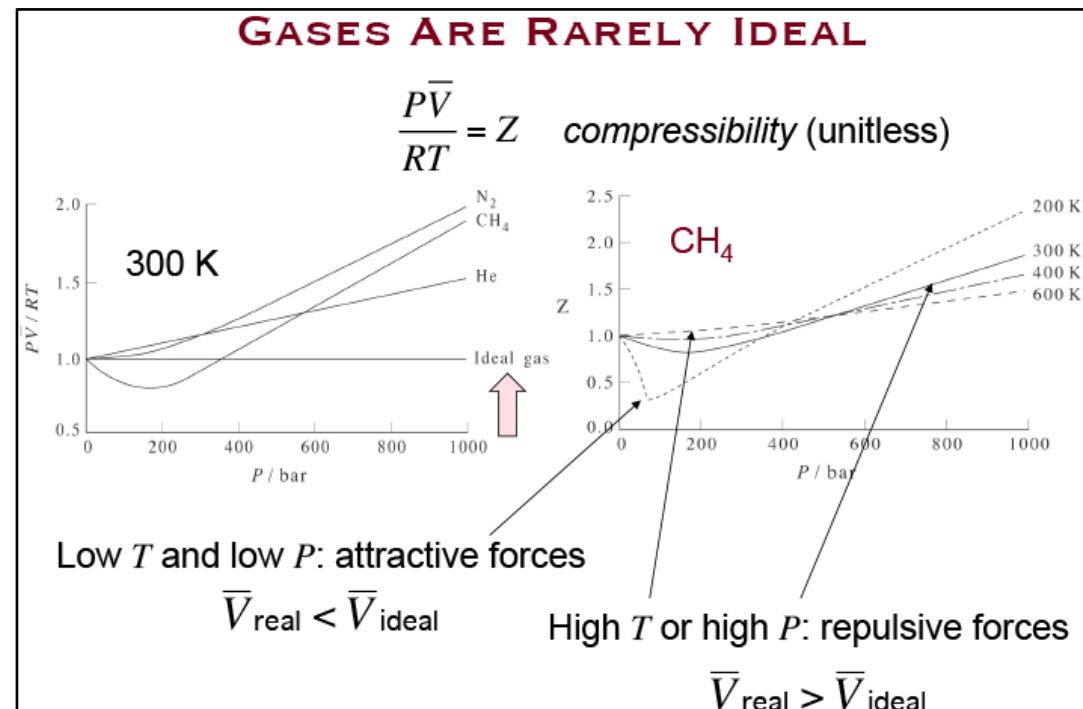
$\boxed{Z < 1 \text{ at low pressure}}$

② High pressure region
 V is small, $P > \frac{a}{V^2}$

$$P(V-b) = RT$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$\boxed{Z > 1 \text{ at high pressure}}$



(3) Low pressure and high Temp, $PV = RT$

Pure Substances:

Cannot be separated into similar substances by chemical or physical means.

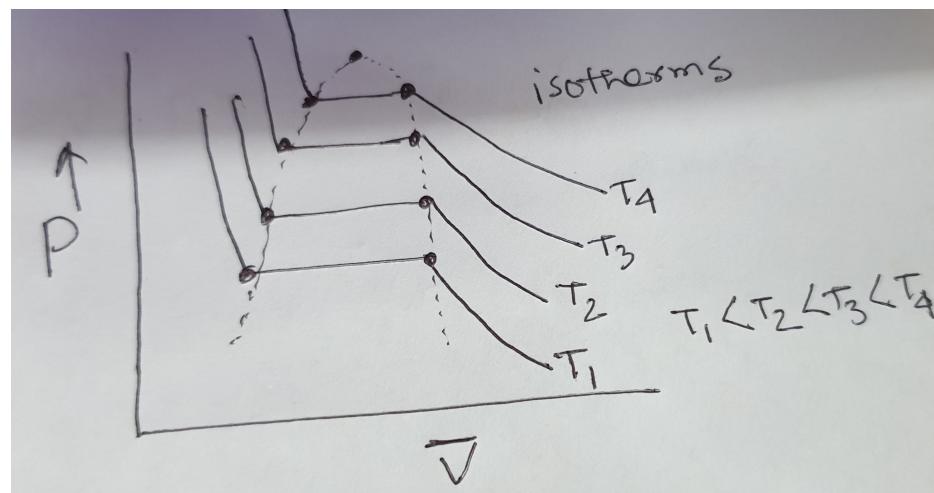
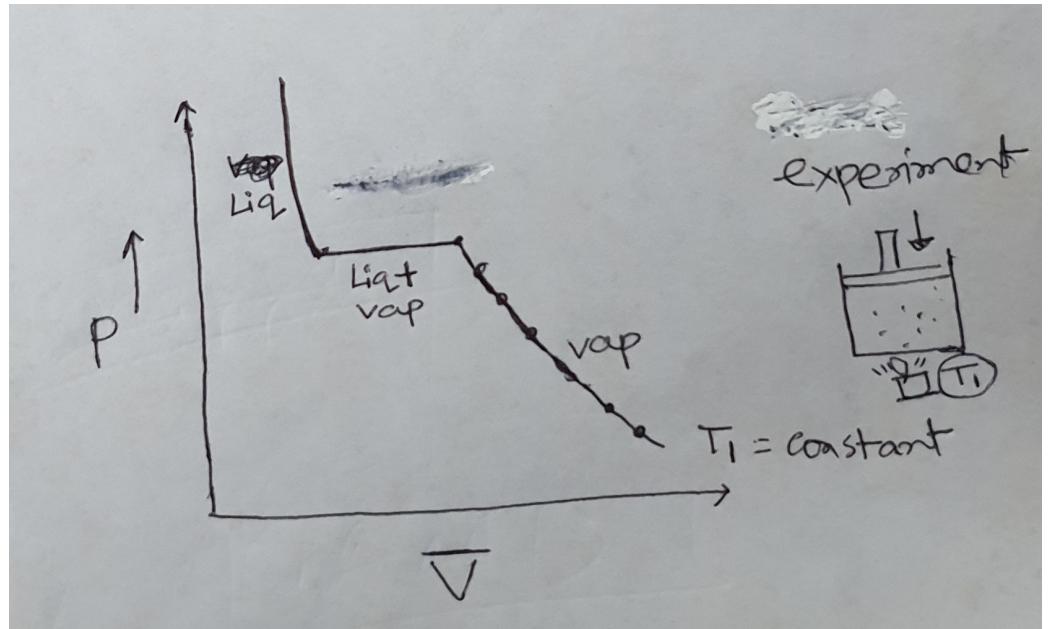
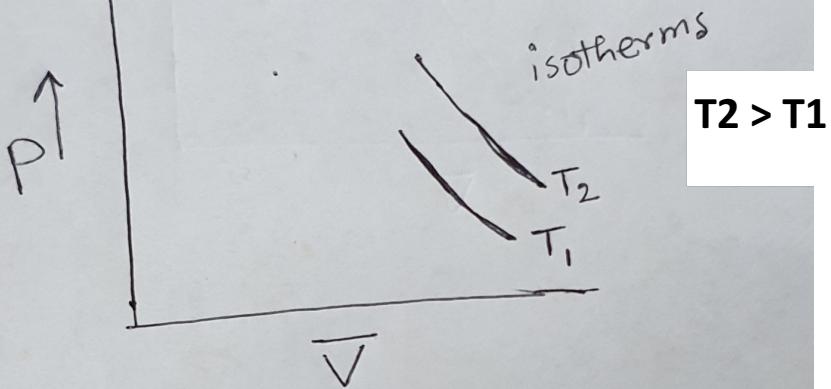
Phases:

1. Solid
2. Liquid
3. Vapor/gas
4. Mixture of above

$$P\bar{V} = RT$$

$$\bar{V} = \frac{V}{n}$$

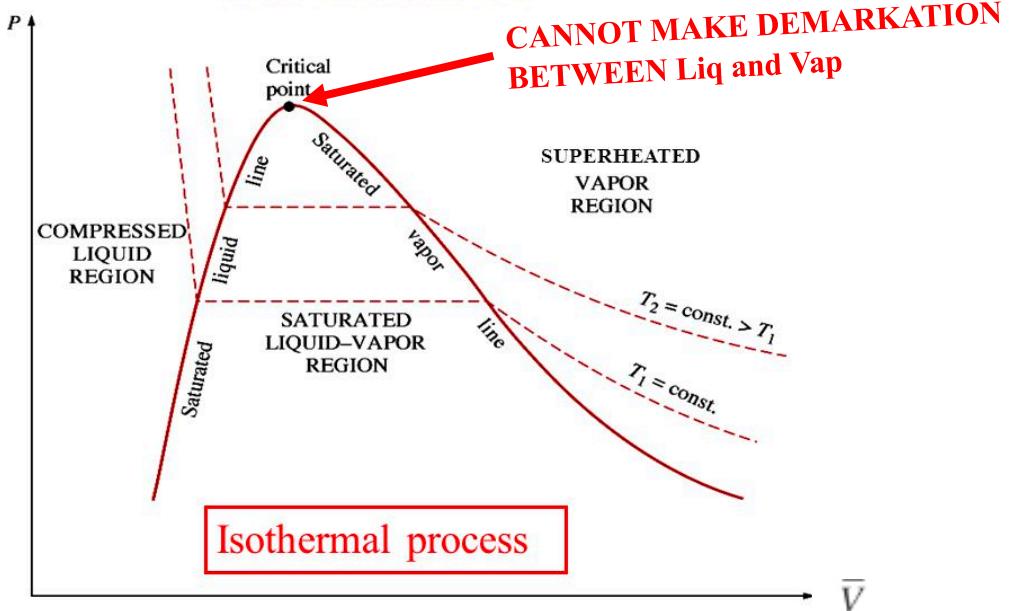
↑
molar volume



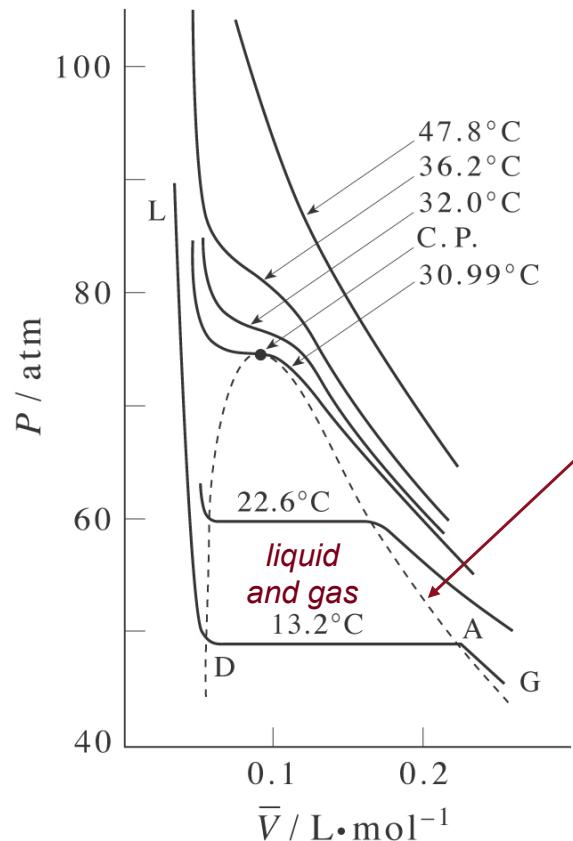
Observations:

1. Saturate vapour line
2. Saturated Liquid Line
3. Liquid-Vapour coexistence region (Horizontal line)
4. Critical point

P- \bar{V} Diagram of a Pure Substance



PV DIAGRAM FOR CARBON DIOXIDE



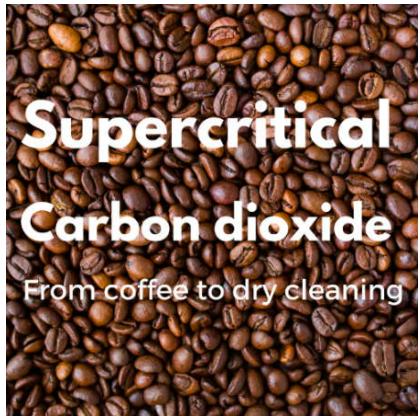
Isotherms
(plots of P vs \bar{V} at constant T)

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



APPLICATION OF SUPERCRITICAL CO₂

DECAFFEINATE
COFFEE ?

DRY
CLEANIN



?

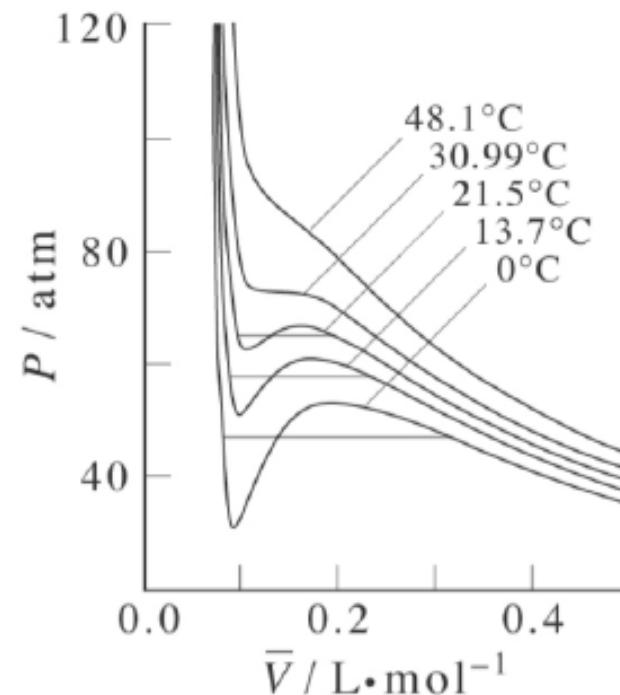
Unravelling the Decaffeination mystery
-Organic CO₂ process

First Published - April 18, 2018 (By Rudy - Cupping Guru)

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attachments.zip

NON-IDEAL CUBIC EQUATIONS OF STATE



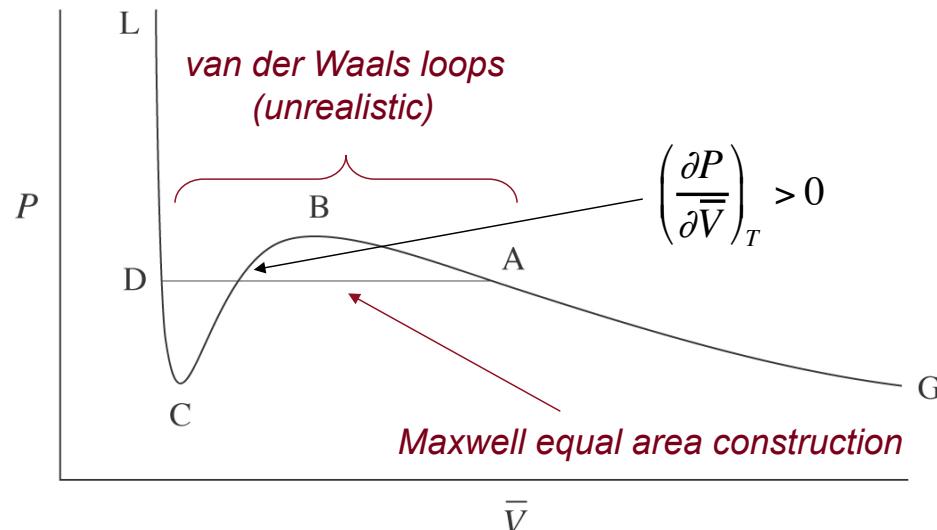
van der Waals EOS

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

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

VDW CUBIC EQUATION OF STATE

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



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

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:

$$(\bar{V} - \bar{V}_c)^3 = 0$$

SOLUTION FOR THE CRITICAL ISOTHERM

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

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

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

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

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

Lecture - 1

VARIOUS CUBIC EQUATIONS OF STATE

van der Waals
$$P = \left(\frac{RT}{\bar{V} - b} \right) - \left(\frac{a}{\bar{V}^2} \right)$$

Redlich-Kwong
$$P = \left(\frac{RT}{\bar{V} - B} \right) - \left(\frac{A}{T^{1/2} \bar{V} (\bar{V} + B)} \right)$$

Peng-Robinson
$$P = \left(\frac{RT}{\bar{V} - \beta} \right) - \left(\frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)} \right)$$



Meghnad Saha
(1893- 1956)

SAHA-BASU EQUATION OF STATE

$$P = - \frac{RT}{2b} \ln \left(1 - \frac{2b}{V} \right) e^{-\frac{a}{RTV}}$$

Critical constants of Saha-Basu equation of state

$$P_C = \frac{a}{4 b^2 e e}$$

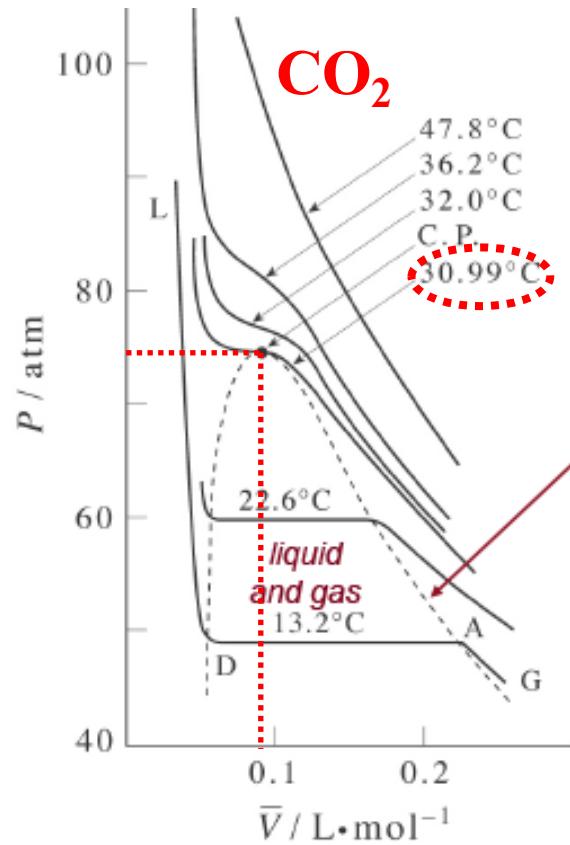
$$V_C = \frac{2eb}{(e-1)}$$

$$T_C = \frac{a}{2ebR}$$

From SAHA-BASU “EOS”:
One can derive
Van der Waals,
Dietrichi equation of state



Satyendra Nath Bose
(1894- 1974)



CRITICAL COMPRESSIBILITY

TABLE 2.5

The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\bar{V}_c/\text{L} \cdot \text{mol}^{-1}$	$P_c \bar{V}_c / RT_c$
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

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

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

A REDUCED EQUATION OF STATE

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \quad \bar{V}_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR}$$



$$\left(P_R + \frac{3}{\bar{V}_R^2}\right)\left(\bar{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R \quad P_R = \frac{P}{P_c} \quad \bar{V}_R = \frac{\bar{V}}{\bar{V}_c} \quad T_R = \frac{T}{T_c}$$

universal equation for *all* gases

reduced quantities

This is an example of the **Law of Corresponding States**:
all gases have the same properties if compared at
corresponding conditions.



Next (L3): Law of Corresponding States Virial Equation of state