CHAPTER 3 – VOLUMETRIC PROPERTIES OF PURE FLUIDS

EQUATIONS OF STATE

$$V = f(P, T) = \frac{1}{\rho}$$

Molar Volume

Pressure

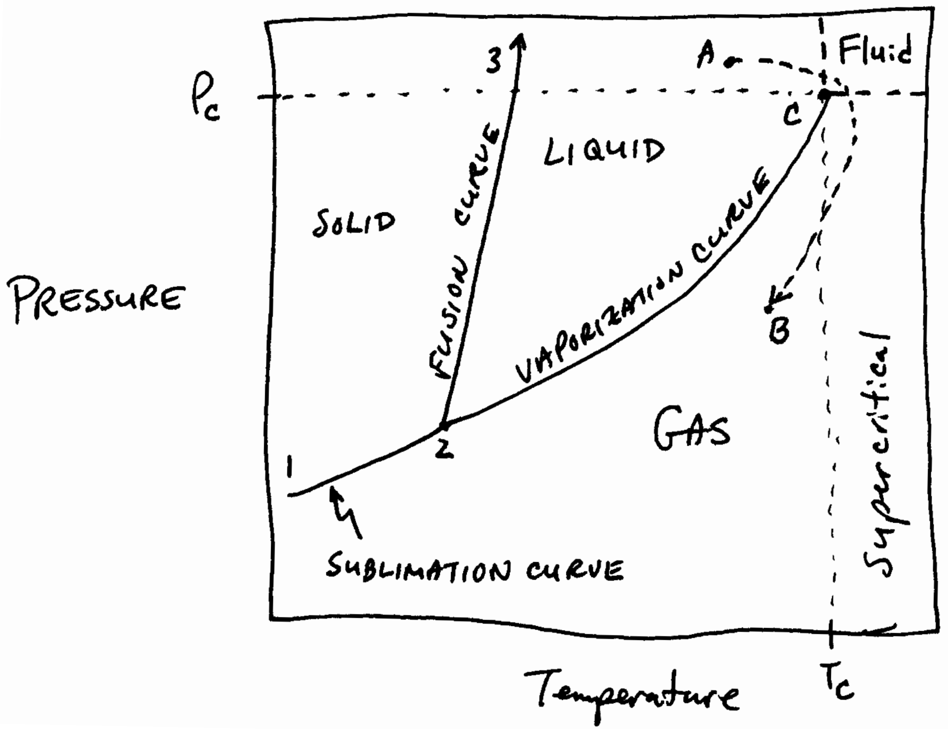
Temperature

Molar Density

EXAMPLE: $PV = RT$ IDeal Gas Law

3.1 PVT Behavior of Pure Substances

FIGURE 3.1



PT DIAGRAM FOR A PURE SUBSTANCE

(Lines are phase boundaries)

Notes:

Line 1-2	SVE	} Vapor Pressure v/s Temperature Lines
Line 2-C	VLE	
Line 2-3	SLE	
Point C	Critical Point (T_c, P_c) Highest point for VLE.	
Point 2	Triple Point Three phases in equilibrium	

Phase Rule:

- At triple point:

$\Pi = 3$, $C = 1$ $\Rightarrow$ $F = 2 - 3 + 1 = 0$

$\Rightarrow$ No properties can change. $\Rightarrow$ Unique set of conditions for the triple point.

- Along Sublimation, Fusion, or Evaporation curves

$\Pi = 2$, $C = 1$ $\Rightarrow$ $F = 2 - 2 + 1 = 1$

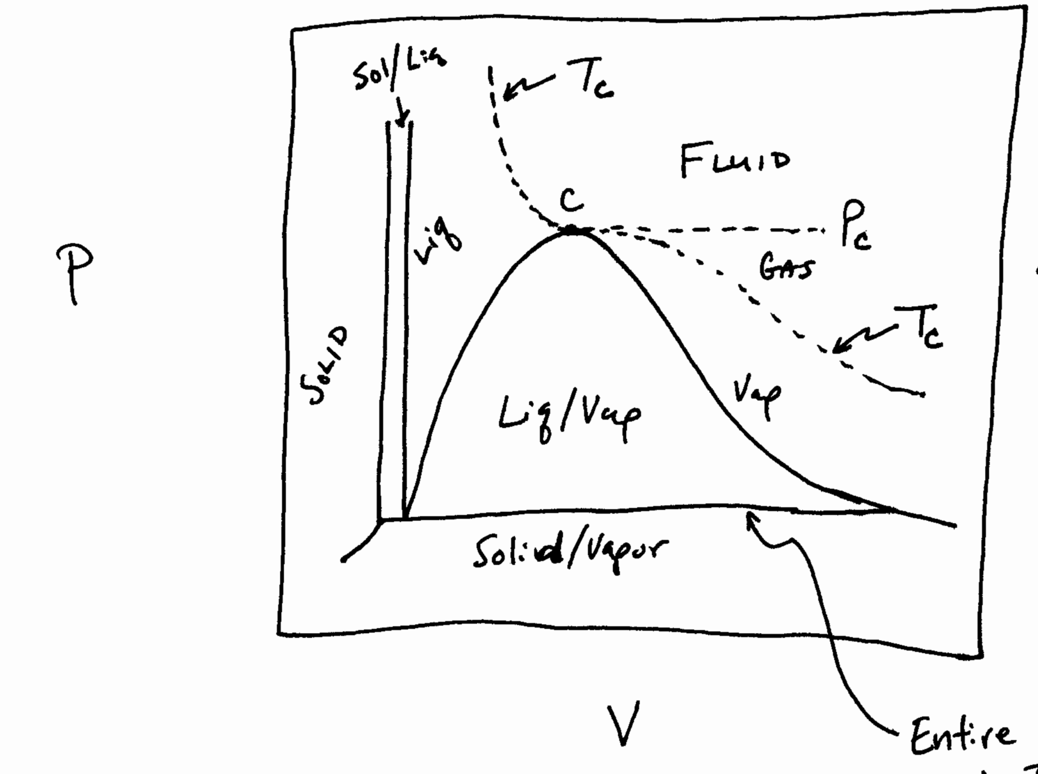
⇒ Need to set one parameter.

- Elsewhere...

$\Pi = 1, \ C = 1 \Rightarrow F = 2 - 1 + 1 = 2$

⇒ Need to set two parameters.

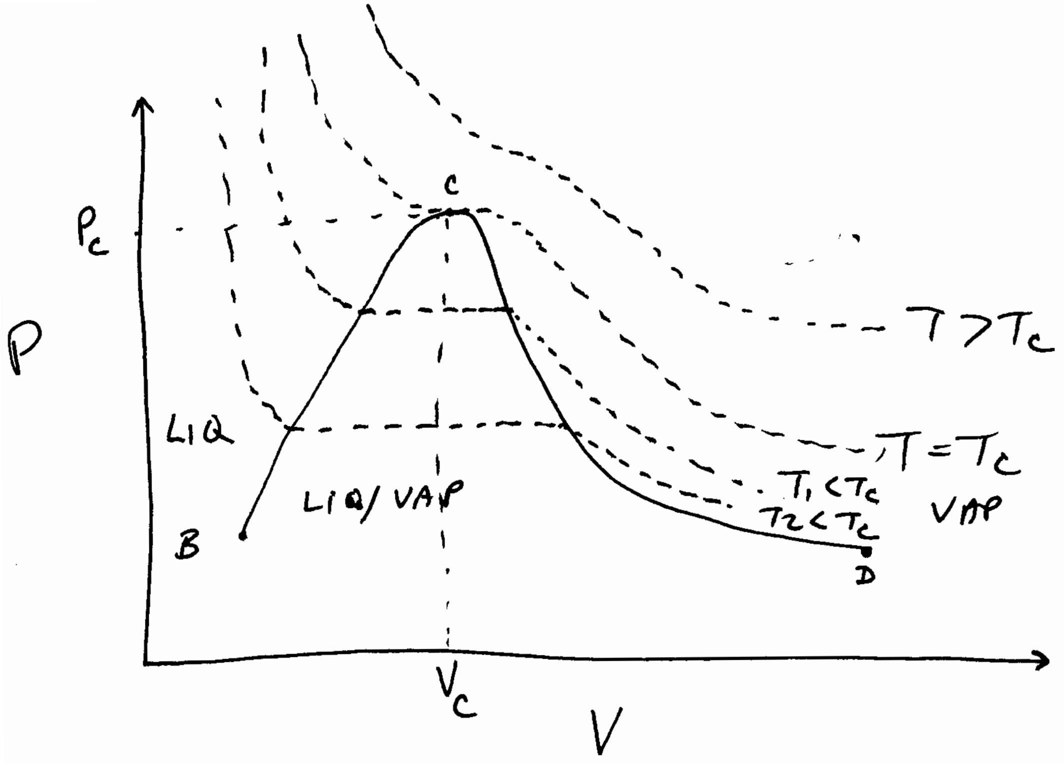
PV DIAGRAM



- LINES ARE SINGLE PHASES
- REGIONS ARE PHASES

Entire Horizontal Line is Triple point.

How do isotherms (constant T lines) from PT diagram map onto PV diagram?



T_1 + T_2 are subcritical temperatures.

Horizontal segments are mixtures of vapor + liquid at <u>constant pressure</u>.

BCD Envelope ⇒ Two phase Region

BC Curve ⇒ Saturated Liquid

CD Curve ⇒ Saturated Vapor

Horizontal lines connecting points on BC + CD are vapor pressures, or saturation pressures.

Left of BC ⇒ Subcooled Liq. ($T < T_{BP}$)

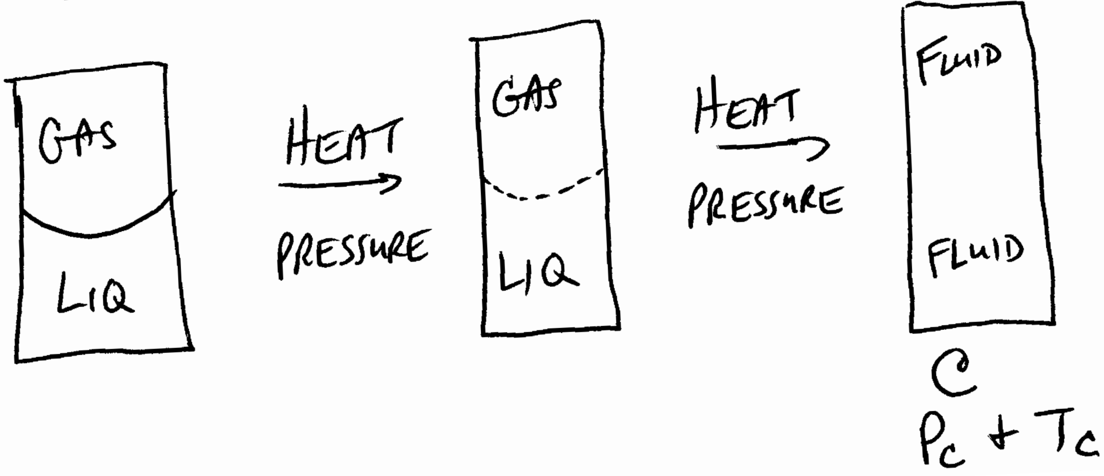
Right of CD ⇒ Superheated Vapor ($T > T_{BP}$)

Isotherms in subcooled Liquid are very steep. (ρ_{LIQ} not strong function of P)

CRITICAL BEHAVIOR;

→ Looking at the critical point.

Can no longer see a differences between Liquid + Gas Phases.



SINGLE PHASE REGION:

FLUID REGION — P, V, and T Related

$$f(P, V, T) = 0 \quad \text{(PVT EQN. OF STATE)}$$

EXAMPLE: Low Pressure GAS

IDEAL GAS LAW ($PV = RT$) (more detail later)

In general, an equation of state may be solved for P, V, or T in terms of the other two quantities,

$$\text{So,} \quad P = f(V, T)$$
$$V = f(P, T)$$
$$T = f(P, V)$$

Example: $V = f(P, T)$

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

These have physical significance.

Volume Expansivity:

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

Volume changes
w/ T @ constant P

Isothermal Compressibility

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

Volume changes
w/ P @ constant T.

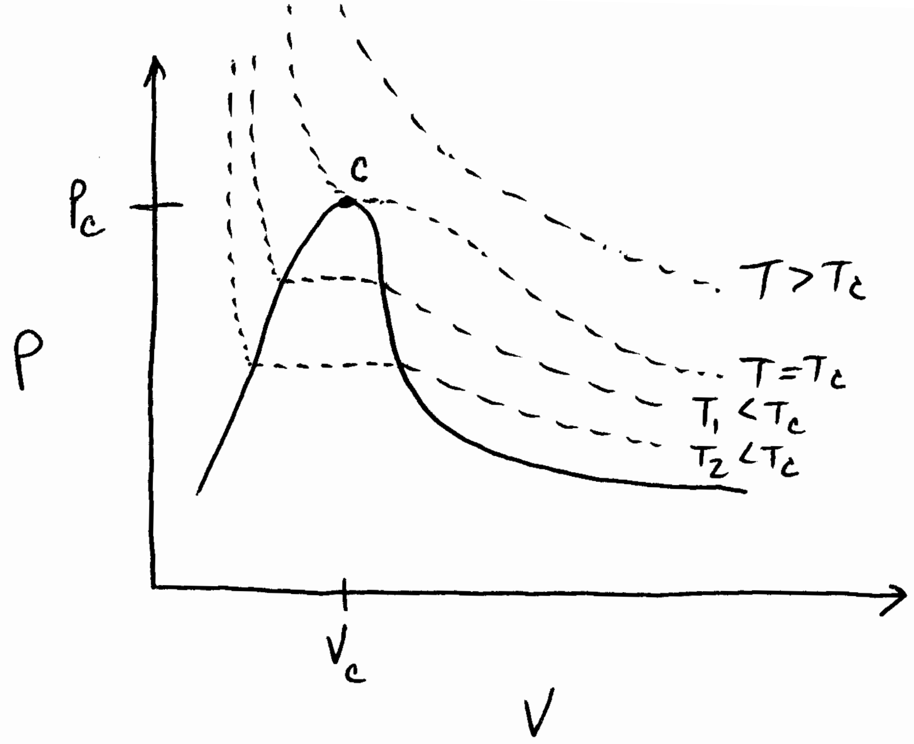
Now, substitute ...

$$\frac{1}{V}\left(dV\right) = \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]\frac{1}{V}$$

$$\frac{dV}{V} = \left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]dT - \left[-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

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

How does this
apply to
Figure 3.2?



Two Cases:

$V < V_c$

$\left(\frac{\partial V}{\partial P}\right)_T$ very small (Slope)

$\left(\frac{\partial V}{\partial T}\right)_P$ very small (isotherms closely spaced)

But here fluid behaves like liquid.

$\Rightarrow$ INCOMPRESSIBLE

$\Rightarrow \beta = 0$ No volume change w/ Pressure

$\Rightarrow K = 0$ No volume change w/ Temperature

(IDEAL CASE)

OF COURSE, NO REAL FLUID IS INCOMPRESSIBLE

GENERAL TRENDS:

1) FOR LIQUIDS, $\beta > 0$ ($V\uparrow$ as $T\uparrow$)

(Exception: Water @ 0-4°C)

2) $K > 0$ ($V\downarrow$ as $P\uparrow$)

Why? $\underline{\underline{\text{COMPRESSIBLE}}}$

If away from critical point,

β & $K \approx$ constant

for small changes in P & T. $\Rightarrow$

$$\int_{V_1}^{V_2} \frac{dV}{V} = \int_{T_1}^{T_2} \beta \, dT - \int_{P_1}^{P_2} K \, dP$$

$$\ln V \Big|_{V_1}^{V_2} = \beta (T_2 - T_1) - K (P_2 - P_1)$$

$$\boxed{\ln\left(\frac{V_2}{V_1}\right) = \beta (T_2 - T_1) - K (P_2 - P_1)}$$

EXAMPLE 3.1 For liquid acetone @ 20°C + 1 bar

$\beta = 1.487 \times 10^{-3} / {}^\circ C$

$K = 62 \times 10^{-6} / \text{bar}$ $\qquad V = 1.287 \frac{cm^3}{g}$

For acetone, find:

(a) $\left(\frac{\partial P}{\partial T}\right)_V$ @ 20°C + 1 bar

(b) P generated by heating at constant V from 20°C and 1 bar to 30°C.

(c) The change in volume for a change from 20°C and 1 bar to 0°C and 10 bar.

(a) $\left(\frac{\partial P}{\partial T}\right)_V$:

$$\frac{dV}{V} = \beta\, dT - K\, dP \qquad @\ dV=0$$

$$0 = \beta\, dT - K\, dP \qquad \text{Solve for } \frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{\beta}{K} = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{Plug + Chug}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1.487\times10^{-3}}{°C}\bigg|\frac{\text{bar}}{62\times10^{-6}} = 23.98\ \frac{\text{bar}}{°C}$$

(b) At constant volume

$$\int_{1\,\text{bar}}^{P} dP = 23.98\,\frac{\text{bar}}{°C}\int_{20°C}^{30°C} dT$$

$$P - 1\,\text{bar} = 23.98\,\frac{\text{bar}}{°C}\,(10°C) \Rightarrow \boxed{P = 240.8\,\text{bar}}$$

(c) $$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

Plug & Chug

$$\ln\left(\frac{V_2}{1.287}\right) = \frac{1.487 \times 10^{-3}}{{}^\circ C}(0 - 20)^\circ C - \frac{62 \times 10^{-6}}{bar}(10 - 1)\ bar$$

$$\frac{V_2}{1.287} = \exp(-0.0303)$$

$$\boxed{V_2 = 1.249\ \frac{cm^3}{g}}$$ So, $$\boxed{\Delta V = -0.038\ \frac{cm^3}{g}}$$

($\Rightarrow$ Essentially incompressible for liquid.)

Not the case for gases & vapors.

$\boxed{3.2}$ Virial Equations of State

Recall Fig. 3.2b
for $V > V_c$

Isotherms are
very smooth
curves.

⇒ Should be able
to use curve fitting.

NOTE: $P \uparrow$ as $V \downarrow$

There fore $PV \approx$ constant for constant T.

⇒ Power Series

$$PV = a + bP + cP^2 + \ldots$$

or

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

Normally truncated after first two terms.

Parameters B', C', D', etc. are temperature and chemical species dependent.

However, "a" is universal, for each temperature.

$$\Rightarrow \underbrace{(PV)^*}_{@\ P\to 0} = a = f(T)$$

(See Power Series)

Think <u>Ideal Gas</u>

$$(PV)^* = a = RT$$

At the triple point of water

$$(PV)^*_t = 22{,}711.8\ \frac{\text{cm}^3\ \text{bar}}{\text{mol}}$$

$$T = 273.16\text{K}$$

Plug & Chug & Solve for R

$$\boxed{R = 83.1447\ \frac{\text{cm}^3\ \text{bar}}{\text{mol}\cdot\text{K}}}$$

See App. A
Table A.2
for other
units.

So, Virial equation state becomes;

$$\boxed{PV = RT\left(1 + B'P + C'P^2 + D'P^3 + \dots\right)}$$

Next, COMPRESSIBILITY FACTOR:

$$Z = \frac{PV}{RT} \Rightarrow PV = ZRT$$

So, $Z = 1 + B'P + C'P^2 + D'P^3 + \dots$

OR

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

$B \neq B'$ (Second Virial Coefficients)

$C \neq C'$ (Third Virial Coefficients)

See p. 72 Smith & Van Ness for how B, B', C, C', etc. are related.

A few more notes about virial coefficients.

→ $\frac{B}{V}$ Related to interactions between pairs of molecules.

→ $\frac{C}{V^2}$ Related to 3-body interactions.

Higher order interactions less & less frequent. Hence, we ignore these terms.

3.3 THE IDEAL GAS

$V \to \infty$ or $P \to 0$

$\Rightarrow$ No interactions.

$$\Rightarrow \frac{B}{V} \to 0, \quad \frac{C}{V^2} \to 0, \text{ etc,}$$

$$Z \to 1 \quad \& \quad \boxed{PV = RT}$$

Also for ideal gas,

$$U = U(T) \text{ only.}$$

So, recall some other property relations:

$$C_v \equiv \left(\frac{\partial U}{\partial T}\right)_v = \frac{dU(T)}{dT} = \underset{\text{only}}{f(T)}$$

$$H = U + PV = \boxed{U(T) + RT = \underset{\text{only}}{H(T)}}$$

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p = \frac{dH(T)}{dT} = \underset{\text{only}}{f(T)}$$

$$C_p = \frac{d}{dT}\left(U(T) + RT\right) = \underbrace{\frac{dU(T)}{dT}}_{C_v} + R$$

$$\Rightarrow \boxed{C_p = C_v + R}$$ FOR IDEAL GAS

(BUT ONLY IG UP TO ~5 bar)

EQUATIONS FOR PROCESS CALCULATIONS FOR IDEAL GASES

→ HEAT (Q)

→ WORK (W)

Mechanically reversible, closed system

$$dW = -m P dV$$

if $m = 1$ kg,

$$\boxed{dW = -P dV}$$

FIRST LAW, CLOSED SYSTEM

$$dU = \underbrace{dQ + dW = C_V dT}_{}$$

Substitute for dW + solve for dQ:

$$\boxed{dQ = C_V dT + P dV}$$

CAN SOLVE FOR dQ OR dW IN TERMS OF TWO PARAMETER OUT OF P, V, AND T BY SUBSTITUTION FROM THE IDEAL GAS LAW.

<u>Example</u>: $P = \frac{RT}{V}$

$$dQ = C_V dT + RT\frac{dV}{V}$$

$$dW = -RT\frac{dV}{V}$$

<u>Example</u>: $V = \frac{RT}{P}$

$$dQ = C_V dT + P\,dV$$

$$= C_V dT + P\,d\left(\frac{RT}{P}\right)$$

$$= C_V dT + P\left[\frac{-RT}{P^2}dP + \frac{R}{P}dT\right]$$

$$= C_V\,dT - RT\,\frac{dP}{P} + R\,dT$$

$$= (C_V + R)\,dT - RT\,\frac{dP}{P}$$

$$\boxed{dQ = C_P\,dT - RT\,\frac{dP}{P}}$$

$$\boxed{dW = -R\,dT + RT\,\frac{dP}{P}}$$

Example: $T = \frac{PV}{R}$

$$dQ = C_V\,dT + P\,dV$$

$$= C_V\,d\left(\frac{PV}{R}\right) + P\,dV$$

$$= \frac{C_V}{R}\left(P\,dV + V\,dP\right) + P\,dV$$

$$= \left(\frac{C_V}{R} + 1\right)P\,dV + \frac{C_V V}{R}\,dP$$

$$= \left(\frac{C_V}{R} + \frac{R}{R}\right) P\,dV + \frac{C_V V}{R}\,dP$$

$$\boxed{dQ = \frac{C_P}{R} P\,dV + \frac{C_V V}{R}\,dP}$$

$$\boxed{dW = -P\,dV}$$

All for mechanically reversible & closed system.

ISOTHERMAL PROCESS (Constant T)

$U = f(T)$ only $\Rightarrow \Delta U = 0$

$H = f(T)$ only $\Rightarrow \Delta H = 0$

$$dQ = \cancelto{0}{C_V\,dT} + RT\,\frac{dV}{V}$$

or

$$dQ = \cancelto{0}{C_P\,dT} - RT\,\frac{dP}{P}$$

OR INTEGRATED

$$\int dQ = RT\int \frac{dV}{V}$$

$$\boxed{Q = RT \ln \frac{V_2}{V_1}}$$ ISOTHERMAL

$$\int dQ = -RT\int \frac{dP}{P}$$

$$\boxed{Q = -RT \ln \frac{P_2}{P_1}}$$ ISOTHERMAL

$$\Delta U = Q + W = 0$$

$$\Rightarrow Q = -W$$

So, $\boxed{W = -RT \ln \frac{V_2}{V_1}}$

or

$$\boxed{W = RT \ln \frac{P_2}{P_1}}$$

Both for Isothermal.

ISOBARIC PROCESS (Constant P)

$$\Delta U = \int C_v \, dT \qquad \Delta H = \int C_p \, dT$$

$$dQ = C_p \, dT - RT \cancel{\frac{dP}{P}}_{\searrow 0}$$

$$\Rightarrow \boxed{Q = \Delta H = \int C_p \, dT} \quad \text{Constant } P$$

$$dW = -R \, dT + RT \cancel{\frac{dP}{P}}_{\searrow 0}$$

Integrate:

$$W = -R \int_{T_1}^{T_2} dT$$

$$\boxed{W = -R\,(T_2 - T_1)} \quad \text{Constant } P$$

ISOCHORIC PROCESS (Constant V)

$$\Delta U = \int C_v \, dT \qquad \Delta H = \int C_p \, dT$$

$$dQ = C_v \, dT + \cancel{RT \frac{dV}{V}} \to 0$$

$$dQ = C_v \, dT$$

Integrate

$$\boxed{Q = \int C_v \, dT = \Delta U}$$ Constant V

$$dW = \cancel{-RT \frac{dV}{V}} \to 0$$

$$\Rightarrow \boxed{W = 0}$$ Constant V

ADIABATIC PROCESS $(dQ = 0)$

(Here special case for C_p + C_V constant)

Example: $$\cancelto{0}{dQ} = C_V\, dT + RT\frac{dV}{V}$$

Separate + Integrate

$$C_V\, dT = -RT\frac{dV}{V}$$

$$\int_{T_1}^{T_2}\frac{dT}{T} = -\frac{R}{C_V}\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V}\ln\left(\frac{V_2}{V_1}\right) = \frac{R}{C_V}\ln\left(\frac{V_1}{V_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{R/C_V}$$

$$\Rightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}}$$

ADIABATIC,
Constant C_V + C_p

Similarly:

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/c_p}} \qquad \boxed{\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{c_p/c_v}}$$

Let $\gamma = \dfrac{c_p}{c_v}$

So, $\dfrac{R}{c_v} = \dfrac{\overbrace{R+c_v} - c_v}{c_v} = \dfrac{c_p}{c_v} - 1 = \gamma - 1$

AND $\dfrac{R}{c_p} = \dfrac{\overbrace{R+c_v} - c_v}{c_p} = 1 - \dfrac{c_v}{c_p} = \dfrac{\gamma}{\gamma} - \dfrac{1}{\gamma}$

$$= \frac{\gamma-1}{\gamma}$$

<u>SUBSTITUTE</u> (INTO PREVIOUS THREE EQUATIONS)

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = \text{Constant}$$

$$T_2 P_2^{(1-\gamma)/\gamma} = T_1 P_1^{(1-\gamma)/\gamma} = \text{Constant}$$

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} = \text{Constant}$$

$$W = \Delta U \qquad (dQ=0)$$

So, $\boxed{W = C_v \Delta T}$ ← CAN ALSO PUT IN TERMS OF γ. (p. 78)

POLYTROPIC PROCESSES (More generalized)

$$P V^{\delta} = \text{Constant}$$

$$T V^{\delta-1} = \text{Constant}$$

$$T P^{(1-\delta/\delta} = \text{Constant}$$

$$W = \frac{R T_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

$$Q = \frac{(\delta-\gamma) R T_1}{(\delta-1)(\gamma-1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$

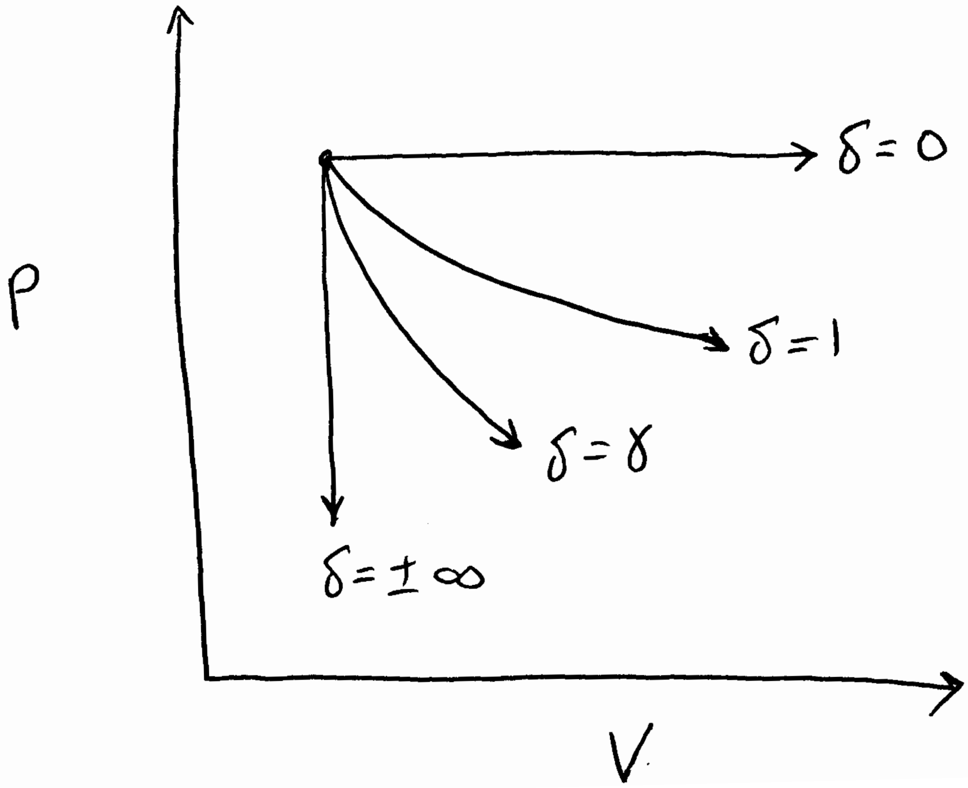
Then convert Polytropic to Specialized:

Isothermal: $\delta = 1$

Isobaric: $\delta = 0$

Isochoric: $\frac{dV}{dP} = \frac{V}{P\delta} \Rightarrow \delta = \pm\infty$

Adiabatic: $\delta = \gamma$



IRREVERSIBLE PROCESS

$$\left.\begin{array}{l} dU \\ dH \\ \Delta U \\ \Delta H \end{array}\right\}$$ SAME EQUATIONS APPLY.

(CLOSED, OPEN, REVERSIBLE, IRREVERSIBLE)

HOWEVER, Q + W PATH DEPENDENT.

TWO STEPS TO GET WORK...

1) W_{REV}

2) Then apply η (efficiency)

a) If work done by system,

$$W_{ACTUAL} = \eta W_{REV}$$

b) If work done on system,

$$W_{ACTUAL} = \frac{W_{REV}}{\eta}$$

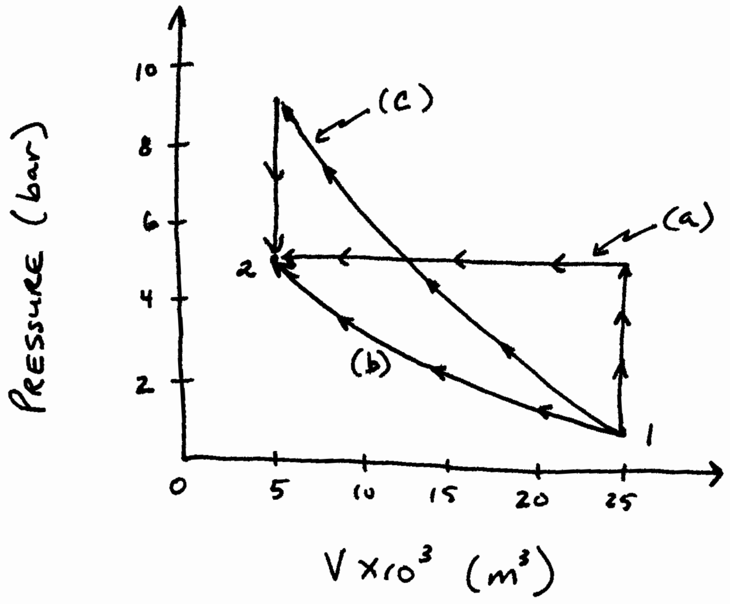
EXAMPLE 3.2 Air is compressed from an initial state of 1 bar and 25°C to a final state of 5 bar and 25°C by three different mechanically reversible processes in a closed system:

(a) Heating at constant volume followed by cooling at constant P.

(b) Isothermal compression.

(c) Adiabatic compression followed by cooling at constant volume.

Assume air to be an ideal gas with the constant heat capacities, $C_V = \frac{5}{2}R$ and $C_P = \frac{7}{2}R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.



GOING FROM STATE ①
TO STATE ②

THREE PATHS.

BASIS: 1 mol air

for $R = 8.314 \frac{J}{mol \cdot K}$ $\Rightarrow$ $C_V = 20.785 \frac{J}{mol \cdot K}$

$C_P = 29.099 \frac{J}{mol \cdot K}$

Ideal Gas:

$$V = \frac{nRT}{P} \Rightarrow V_1 = \frac{8.314\ \text{J}}{\text{mol}\cdot\text{K}}\left|\frac{1\ \text{mol}}{1}\right|\frac{298.15\ \text{K}}{1}\left|\frac{1}{1\ \text{bar}}\right.$$

$$\left|\frac{1.0133\ \text{bar}}{101.33\ \text{kPa}}\right|\frac{1\ \text{kPa}}{10^3\ \text{Pa}}\left|\frac{1\ \text{Pa}\cdot\text{m}^2}{1\ \text{N}}\right|\frac{1\ \text{N}\cdot\text{m}}{1\ \text{J}}$$

$$\boxed{V_1 = 0.02479\ \text{m}^3}$$

V_2 @ same T, but P = 5 bar

$$\Rightarrow \boxed{V_2 = 0.00496\ \text{m}^3}$$

$U = f(T)$ only (Ideal gas)

$$T_1 = T_2 \Rightarrow \boxed{\Delta U = 0}$$

$H = f(T)$ only (Ideal gas)

$$T_1 = T_2 \Rightarrow \boxed{\Delta H = 0}$$

(a)

Rest same as Example 2.9 (b)

$$\Rightarrow \boxed{Q = -9{,}915\ \text{J}}$$

$$\boxed{W = 9{,}915\ \text{J}}$$

(b) Isothermal

$$Q = -W = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1}$$

$$= \frac{8.314\ \text{J}}{\text{mol}\cdot\text{K}} \left| \frac{298.15\text{K}}{1} \right. \ln\left(\frac{0.00496\ \text{m}^3}{0.02479\ \text{m}^3}\right)$$

$$Q = -3989\ \frac{\text{J}}{\text{mol}} \quad \text{or} \quad \boxed{-3989\ \text{J}} \text{ for } 1\text{mol}$$

$$W = -Q \Rightarrow \boxed{W = 3{,}989\ \text{J}}$$

(c) Adiabatic compression followed by cooling at constant volume.

Need intermediate temperature (+ know V_1 + V_2)

$$\frac{T'}{T_1} = \left(\frac{V_1}{V'}\right)^{\gamma - 1} \qquad \text{where } \gamma = \frac{c_p}{c_v} = 1.4$$

$$T' = (298.15\text{K})\left(\frac{0.02479\ \text{m}^3}{0.00496\ \text{m}^3}\right)^{1.4-1} = 567.48\ \text{K}$$

$Q = 0$ (adiabatic compression)

$$W = nC_v\Delta T = \frac{20.785\ \text{J}}{\cancel{\text{mol}}\cdot\text{K}}(567.48 - 298.15)\text{K}\,(1\cancel{\text{mol}})$$

$\boxed{W = 5{,}598\ \text{J}}$ (adiabatic compression)

Constant Volume Step:

$$W = \int -P\,dV = 0$$

$$Q = n C_V \Delta T = (1\,\text{mol})\left(\frac{20.785\,\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 - 567.48)\,\text{K}$$

$$\boxed{Q = -5{,}598\,\text{J}}$$

Overall: $\boxed{Q = -5{,}598\ \text{J}}$ $\boxed{W = 5{,}598\ \text{J}}$ (c)

⇒ MAKES SENSE (LOOK AT AREA UNDER VARIOUS PATHS)

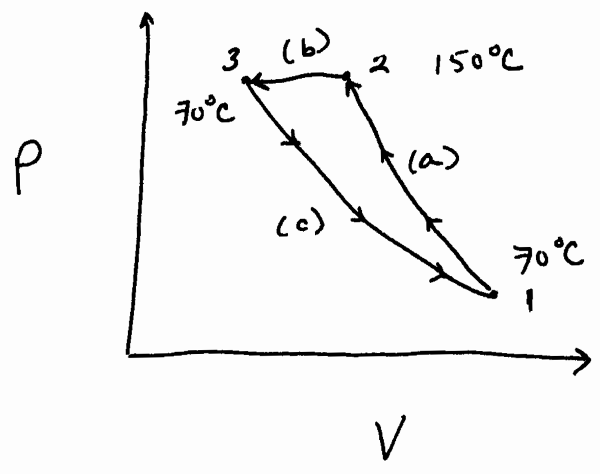
EXAMPLE 3.3 An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(a) From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150°C.

(b) It is then cooled from 150°C to 70°C at constant P.

(c) Finally it is expanded isothermally to its original state.

Calculate W, Q, ΔU, and ΔH for each process & the entire cycle. Take $C_V = \frac{3}{2}R$ & $C_P = \frac{5}{2}R$.



(a) adiabatic compression

(b) isobaric cooling

(c) isothermal expansion

$R = 8.314 \frac{J}{mol \cdot K}$

<u>Basis:</u> 1 mol gas

$C_V = 12.471 \frac{J}{mol \cdot K}$

$C_p = 20.785 \frac{J}{mol \cdot K}$

(a) $\boxed{Q = 0}$ adiabatic

$W = \Delta U = C_V \Delta T$ Plug + Chug

$$W = \Delta U = 12.471 \frac{J}{mol \cdot K} (150 - 70)^{\circ}C \left| \underbrace{\frac{1 K}{1^{\circ}C}}_{\text{ok for } \Delta T} \right| 1 \, mol$$

$$\boxed{W = \Delta U = 998 \, J}$$

$\Delta H = n C_p \Delta T$ (ideal gas)

$$= (1 \, mol)\left(20.785 \frac{J}{mol \cdot K}\right)(150 - 70)^{\circ C} \left| \underbrace{\frac{1 K}{1^{\circ}C}}_{\text{ok for } \Delta T} \right.$$

$$\boxed{\Delta H = 1{,}663\,\text{J}}$$

for adiabatic compression,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_p} \Rightarrow P_2 = P_1\left(\frac{T_2}{T_1}\right)^{C_p/R}$$

$$P_2 = (1\ \text{bar})\left(\frac{150+273.15}{70+273.15}\right)^{\frac{5}{2}\left(\frac{R}{R}\right)} = \boxed{1{,}689\ \text{bar} = P_2}$$

(b) Cooling at constant pressure

$$\Delta U = nC_v\,\Delta T \quad (\text{ideal gas})$$

$$= (1\ \text{mol})\left(\frac{12.471\ \text{J}}{\text{mol}\cdot\text{K}}\right)\underbrace{(70-150)\,^{\circ}\text{C}\,\Big|\,\frac{1\,\text{K}}{1\,^{\circ}\text{C}}}_{\Delta T\ \text{so ok}}$$

$$\boxed{\Delta U = -998\,\text{J}}$$

$$\Delta H = Q = n\,C_p\,\Delta T \quad (\text{ideal gas})$$

$$= (1\ \text{mol})\left(\frac{20.785\ \text{J}}{\text{mol}\cdot\text{K}}\right)\underbrace{(70-150)\,^{\circ}\text{C}\,\Big|\,\frac{1\,\text{K}}{1\,^{\circ}\text{C}}}_{\Delta T,\ \text{so ok}}$$

$$\boxed{\Delta H = Q = -1{,}663\,\text{J}}$$

$$W = \Delta U - Q \quad (\text{closed system})$$

$$= -998\,\text{J} - (-1{,}663\,\text{J}) = \boxed{665\,\text{J} = W}$$

(c) Isothermal expansion

$$\boxed{\Delta U = \Delta H = 0}$$

$$Q = -W = -RT \ln\left(\frac{P_2}{P_1}\right)$$

$$= -\left.\frac{8.314\ J}{mol \cdot K}\right|\left.\frac{1\ mol}{1}\right|\left.\frac{(70+273.15\ K)}{1}\right| \ln\left(\frac{1\ bar}{1.689\ bar}\right)$$

↑ Basis

$$\boxed{Q = 1{,}495\ J}$$

$$\boxed{W = -1{,}495\ J}$$

So, overall:

$\Delta U = 0$ (Should ... but double check)

$\Delta U = 998 J - 998 J + 0 J = \boxed{0 J = \Delta U}$ ✓

$\Delta H = 1{,}663 J - 1{,}663 J + 0 J = \boxed{0 J = \Delta H}$ ✓

$Q = 0 J - 1{,}663 J + 1{,}495 J = \boxed{-168 J = Q}$

$W = 998 J + 665 J - 1{,}495 J = \boxed{168 J = W}$

$\boxed{\text{EXAMPLE 3.4}}$ If the processes of Ex. 3.3 are carried out irreversibly but so as to accomplish exactly the same changes of state (P, T, U, H), then different values of Q + W result. Calculate Q + W if each step is carried out with an efficiency of 80%.

(a) $W_{Rev} = 998\text{ J}$

$\Rightarrow \boxed{W_{ACTUAL} = 1,248\text{ J}}$

Closed System, so $\Delta U = Q + W$

Substitute...

$998\text{ J} = Q + 1,248\text{ J} \Rightarrow \boxed{Q_{ACT} = -250\text{ J}}$

(b) $W_{rev} = 665\text{ J}$

$\Rightarrow \boxed{W_{ACTUAL} = 831\text{ J}}$

$\Delta U = Q + W$

$-998\text{ J} = Q + 831\text{ J} \Rightarrow \boxed{Q_{ACT} = -1,829\text{ J}}$

(c) $W_{rev} = -1,495\text{ J}$

$\Rightarrow W_{ACTUAL} = (-1,495\text{ J})(0.80) = \boxed{-1,196\text{ J} = W_{ACTUAL}}$

SIDEBAR:

WORK DONE ON SYSTEM...

$$W_{ACTUAL} = \frac{W_{REV}}{\eta}$$

TAKES MORE EFFORT

WORK DONE BY SYSTEM ON SURROUNDINGS...

$$W_{ACTUAL} = \eta \cdot W_{REV}.$$

GET LESS THAN YOU CAN THEORETICALLY

Back to Ex. 3.4...

$$\Delta U = Q + W$$

$$0 = Q - 1{,}196\ J \Rightarrow \boxed{Q_{ACT} = 1{,}196\ J}$$

So, entire cycle?

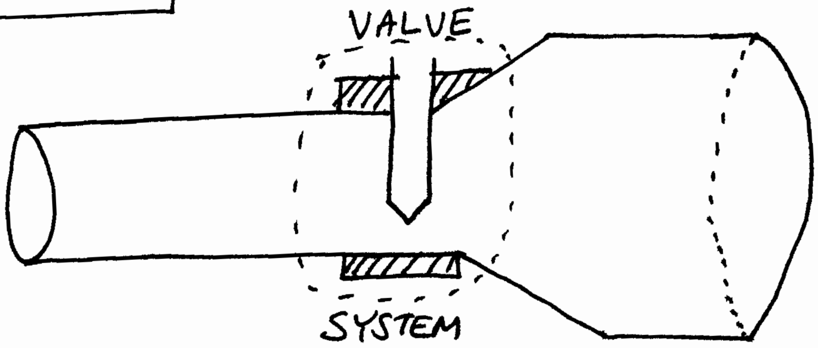
$$Q_{ACT} = -250\ J - 1{,}829\ J + 1{,}196\ J = \boxed{-883\ J}$$

$$W_{ACT} = 1{,}248\ J + 831\ J - 1{,}196\ J = \boxed{883\ J}$$

Same start + end T, so $\Delta U = 0$

$\Rightarrow \boxed{Q = -W}$ (Closed System)

EXAMPLE 3.7



from Ex. 3.6

$Q = 0$, $W_s = 0$

THROTTLE $\Rightarrow \Delta H = 0$

$\Delta E_p \sim 0$ $\quad \Delta E_K \sim 0$ $\quad T_2 = T_1$

ARE THESE REASONABLE ASSUMPTIONS?

$\dot{n}_1 = \dot{n}_2 = 1 \frac{\text{mol}}{\text{s}}$

$D_1 = D_2 = 5\text{cm}$

$\left.\begin{array}{l} \Delta E_K = ? \\ T_2 = ? \end{array}\right\}$

No elevation change. $\Rightarrow \Delta E_p = 0$

$T_1 = 20°\text{C}$ $\quad T_2 = ?$

$P_1 = 6\text{ bar}$ $\quad P_2 = 3\text{ bar}$

Air, Ideal Gas $\quad C_p = \frac{7}{2} R$ $\quad M = 29 \frac{\text{g}}{\text{mol}}$

Recall: $\dot{n} = u A \rho = \frac{u A}{V}$

So, $u = \dfrac{\dot{n}V}{A}$ Need: V + A

$$A = \frac{\pi D^2}{4} = \frac{\pi}{4}(5\,\text{cm})^2 = 19.63\,\text{cm}^2$$

$$V_1 = \frac{RT_1}{P_1} = \frac{83{,}14\ \text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}} \Bigg| \frac{(20+273{,}15)\,\text{K}}{1} \Bigg| \frac{1}{6\ \text{bar}}$$

$$\boxed{V_1 = 4{,}062\ \frac{\text{cm}^3}{\text{mol}}}$$

$$\Rightarrow u_1 = \frac{1\ \text{mol}}{\text{s}} \Bigg| \frac{4{,}062\ \text{cm}^3}{\text{mol}} \Bigg| \frac{1}{19.63\ \text{cm}^2} \Bigg| \frac{1\ \text{m}}{100\ \text{cm}} = \boxed{2.069\ \frac{\text{m}}{\text{s}}}$$

If $\Delta T \sim 0$, then $PV \sim$ constant.

Therefore, when $P_1 = 6$ bar + $P_2 = 3$ bar

then $V_1 = 4{,}062\ \dfrac{\text{cm}^3}{\text{mol}}$ + $\boxed{V_2 = 2V_1 = 8{,}124\ \dfrac{\text{cm}^3}{\text{mol}}}$

$$u_2 = u_1 \Bigg| \frac{V_2}{V_1} = 2u_1 = \boxed{4.138\ \frac{\text{m}}{\text{s}}}$$

So, $\Delta E_K = ?$

$$\Delta E_K = \frac{1}{2}\dot{m}(u_2^2 - u_1^2) = \frac{1}{2}\dot{n}M(u_2^2 - u_1^2)$$

$$= \frac{1}{2}\Big|\frac{1\text{ mol}}{\text{s}}\Big|\frac{29\text{ g}}{\text{mol}}\Big|\frac{(4.138^2 - 2.069^2)\text{ m}^2}{\text{s}^2}\Big|\frac{1\text{ kg}}{10^3\text{ g}}\Big|\frac{\text{s}^2\cdot\text{N}}{1\text{ kg m}}$$

$$\Big|\frac{1\text{ J}}{1\text{ Nm}} = \boxed{0.186\ \frac{\text{J}}{\text{s}} = \Delta E_k}$$

Significant? How much ΔT?

Energy Balance

→ No accumulation → $\Delta z = 0$

→ $Q = 0$ ⇒ $\Delta E_p = 0$

→ $W_s = 0$

$$\Rightarrow \quad \Delta\Big[\big(H + \tfrac{1}{2}u^2\big)\dot{m}\Big]_{fs} = 0$$

$$\dot{m}\,\Delta H\Big| + \frac{1}{2}\dot{m}\,\Delta u^2\Big|_{u_1}^{u_2} = 0$$

Ideal Gas ⇒ $\Delta H = C_p\,\Delta T$

$$\underbrace{\frac{\dot{m}}{M}\,C_p\,\Delta T}_{C_p\text{ was molar quantity}}\Big|_{T_1}^{T_2} + \frac{1}{2}\dot{m}\big(u_2^2 - u_1^2\big) = 0$$

Plug + Chug →

$$\frac{1}{2}\dot{m}\left(u_2^2-u_1^2\right) = 0.186\ \frac{J}{s}$$

$$\frac{\dot{m}}{M} = \dot{n}$$ Substitute & solve for ΔT.

$$\dot{n}\,C_p\,\Delta T + 0.186\ \frac{J}{s} = 0$$

$$\Delta T = \frac{1}{\dot{n}\,C_p}\left(-0.186\ \frac{J}{s}\right)$$

$$= \frac{1\,s}{1\,mol}\left|\frac{2}{7}\right|\frac{mol \cdot K}{8.314\,J}\left|\frac{-0.186\,J}{s}\right.$$

$$\Delta T = \boxed{-0.0064\ K = \Delta T}$$

NO SIGNIFICANT TEMPERATURE CHANGE.

SO, $\underline{\underline{\Delta H = C_p\,\Delta T \approx 0\ J}}$ ✓ GOOD ASSUMPTION

(THROTTLING PROCESS)

$\boxed{3.4}$ APPLICATION OF THE VIRIAL EQUATIONS.

TRUNCATED TO THREE TERMS (IN $1/V$)

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

$B \equiv$ Second Virial Coefficient

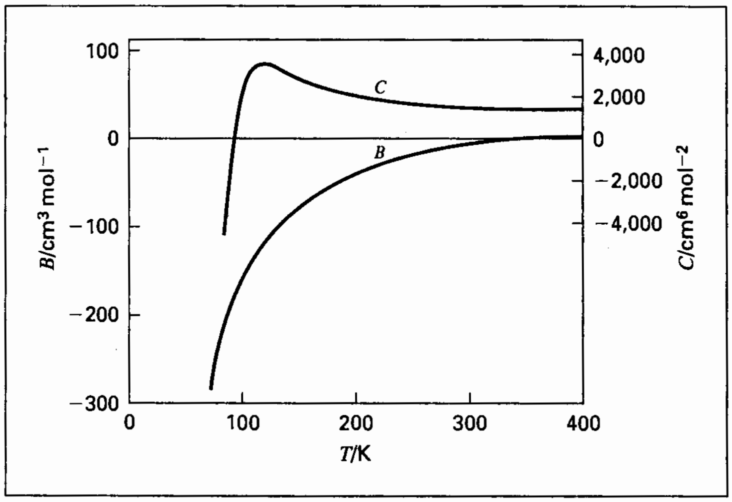
$C \equiv$ Third Virial Coefficient

Where are these tabulated?
(functions of chemical species + Temperature)

→ J. H. Dymond and E.B. Smith, "The Virial Coefficients of Pure Gases and Mixtures," Clarendon Press, Oxford, 1980.

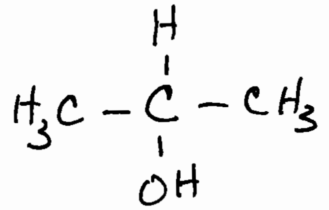
Example:

Figure 3.10
Smith +
Van Ness.



EXAMPLE 3.8 Reported values for the virial coefficients of isopropanol vapor at 200 °C are:

$$B = -388 \frac{cm^3}{mol}$$



$$H_3C-\overset{H}{\underset{OH}{C}}-CH_3$$

isopropanol (IPA)

$$C = -26{,}000 \frac{cm^6}{mol^2}$$

Calculate V + Z for IPA vapor @ 200 °C + 10 bar

by:
(a) Ideal Gas Equation
(b) Equation 3.38
(c) Equation 3.40

$$T = 200 + 273.15 = 473.15\ K$$

$$R = 83.14 \frac{cm^3 \cdot bar}{mol \cdot K}$$

(a) $Z = 1$ (Ideal Gas)

$$1 = \frac{PV}{RT} \Rightarrow V = \frac{RT}{P}$$

Plug + Chug

$$V = \frac{83.14\ cm^3 \cdot bar}{mol \cdot K} \bigg| \frac{473.15\ K}{10\ bar} = \boxed{3{,}934 \frac{cm^3}{mol}}$$ (Ideal Gas)

Next, virial equations →

(b) $\frac{PV}{RT} = 1 + \frac{BP}{RT} \Rightarrow \boxed{V = \underbrace{\frac{RT}{P}}_{V_{ig}} + B}$

$\Rightarrow V = 3{,}934 \frac{cm^3}{mol} + B$

$\Rightarrow V = 3{,}934 + (-388) \Rightarrow \boxed{V = 3{,}546 \frac{cm^3}{mol}}$

$\Rightarrow$ Compressible

$$Z = \frac{PV}{RT} = \frac{10\,bar}{473.15K} \left| \frac{mol \cdot K}{83.14\, cm^3 \cdot bar} \right| \frac{3{,}546\, cm^3}{mol}$$

$\Rightarrow \boxed{Z = 0.9014}$

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

$\Rightarrow V = \frac{RT}{P}\left[1 + \frac{B}{V} + \frac{C}{V^2}\right]$

$\Rightarrow$ Use solver, or iterative method.

$(\underbrace{V_{i+1} - V_i}) \rightarrow 0)$

$$V_{i+1} = \underbrace{\frac{RT}{P}}_{V_{\text{IDEAL GAS}}} \left[1 + \frac{B}{V_i} + \frac{C}{V_i^2} \right]$$

Procedure:

1) Guess V_i

→ Start at $V_i = V_{\text{IDEAL GAS}}$

2) Calculate V_{i+1}

3) $V_{i+1} - V_i$ < tolerance?

→ yes → DONE

→ No → $V_i = V_{i+1}$ + Recalculate.

So, $V_{\text{IDEAL GAS}} = 3{,}934 \frac{\text{cm}^3}{\text{mol}}$ (already calculated)

$$V_{i+1} = 3{,}934 \left[1 - \frac{388}{V_i} - \frac{26{,}000}{V_i^2} \right]$$

i	V_i	V_{i+1}	$V_{i+1} - V_i$
0	3,934	3,539	−395
1	3,539	3,494	−45
2	3,494	3,488	−6

$$V_0 = 3{,}934 \ \frac{cm^3}{mol}$$

$$V_1 = 3{,}934\left[1 - \frac{388}{3934} - \frac{26{,}000}{(3934)^2}\right] = 3{,}539 \ \frac{cm^3}{mol}$$

$$V_2 = 3{,}934\left[1 - \frac{388}{3539} - \frac{26{,}000}{(3539)^2}\right] = 3{,}494 \ \frac{cm^3}{mol}$$

$$V_3 = 3{,}934\left[1 - \frac{388}{3494} - \frac{26{,}000}{(3494)^2}\right] = 3{,}488 \ \frac{cm^3}{mol}$$

$$V_4 = 3{,}934\left[1 - \frac{388}{3488} - \frac{26{,}000}{(3488)^2}\right] = 3{,}488 \ \frac{cm^3}{mol}$$

$$\underline{\underline{V_4 - V_3 = 0}} \quad \Rightarrow \underline{\text{DONE}}$$

$$\boxed{V = 3{,}488 \ \frac{cm^3}{mol}}$$

$$Z = \frac{PV}{RT} = \frac{10\ bar}{473{,}15K}\left|\frac{3{,}488\ cm^3}{mol}\right|\frac{mol \cdot K}{83.14\ cm^3 \cdot bar}$$

$$\boxed{Z = 0.8867}$$

NEXT, CUBIC EQNS. OF STATE.

$\boxed{3.5}$ CUBIC EQUATIONS OF STATE

SIMPLEST EQUATION OF STATE THAT CAN REPRESENT LIQUIDS + VAPORS

(VIRIAL EQUATIONS FOR GASES + VAPORS ONLY)

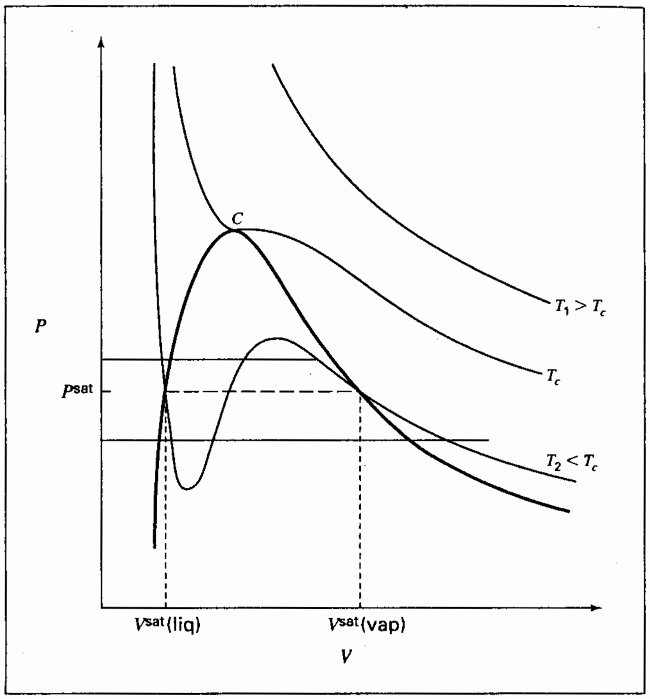
TYPE I: van der Waals EOS

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

both a and b > 0

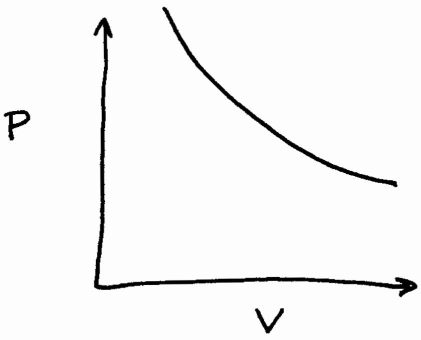
when $a = b = 0$ → Reduces to ideal gas law.

FIG. 3.11



Three isotherms (Constant T curves) on FiG. 3.11:

$T > T_c$:

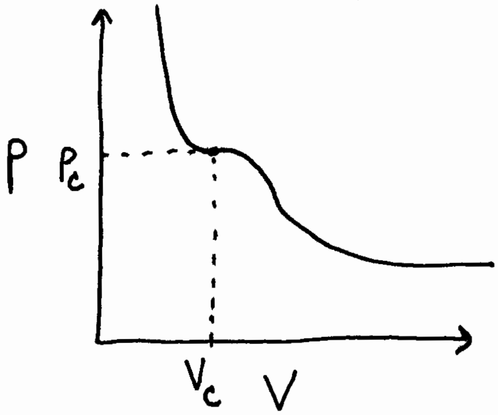


- Smooth Curve
- No maxima
- No minima

Cubic equation has **one** **real** root.
Other two roots are imaginary.

(for any $P > 0$, only one real value of V)

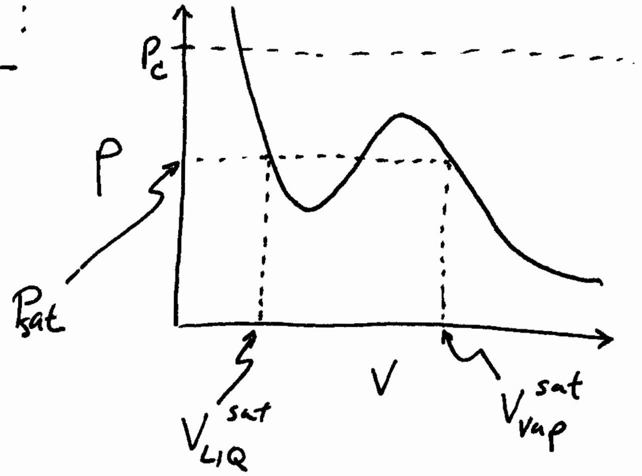
$T = T_c$:



- smooth curve
- No maxima
- No minima
- $\underbrace{\frac{\partial P}{\partial V}}_{\text{Slope}} = 0$ @ V_c

Same for $T > T_c$ except at $P = P_c$,
three real roots all $= V_c$.

$T < T_c$:

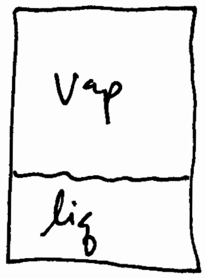


- smooth curve
- local maxima + minima

Experimentally (Real world):

$V_{LIQ}^{sat} < V < V_{vap}^{sat}$ meaningless.

Why?



Two phases and each phase has its own specific volume.

So, in range $V_{LIQ}^{sat} < V < V_{vap}^{sat}$

isotherm is a horizontal line for each pressure (P^{sat}) and temperature (T^{sat}).

(See isotherms on Fig. 3.11)

TYPE II: GENERALIZED CUBIC E.O.S.

$$P = \frac{RT}{V-b} - \underbrace{\frac{\Theta\,(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}}_{\text{Specialization here (tweaking)}}$$

Parameters: $b,\ \Theta,\ \kappa,\ \lambda,\ \eta$

$$\text{all } f(\underset{\substack{\uparrow\\ \text{temperature}}}{T},\ \underbrace{x_i,\ y_i}_{\substack{\uparrow\\ \text{composition}}})$$

Reduces to van der Waals EOS when:

$\eta = b \qquad \Theta = a$

$\kappa = 0 \qquad \lambda = 0$

Really?

$$P = \frac{RT}{V-b} - \frac{a\,\cancel{(V-b)}}{\cancel{(V-b)}(V^2+0+0)} \qquad \checkmark$$

If we substitute:

$\eta = b \qquad \Theta = a(T)$

$\kappa = (\epsilon + \sigma) b \qquad \lambda = \epsilon \sigma b^2$

And factor the denominator, we get the

GENERIC CUBIC EQUATION OF STATE:

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

For a given cubic equation of state:

$$\left.\begin{matrix} \epsilon \\ \sigma \end{matrix}\right\} \text{pure numbers (constant for EOS)}$$

$$\left.\begin{matrix} a(T) \\ b \end{matrix}\right\} \text{substance dependent}$$

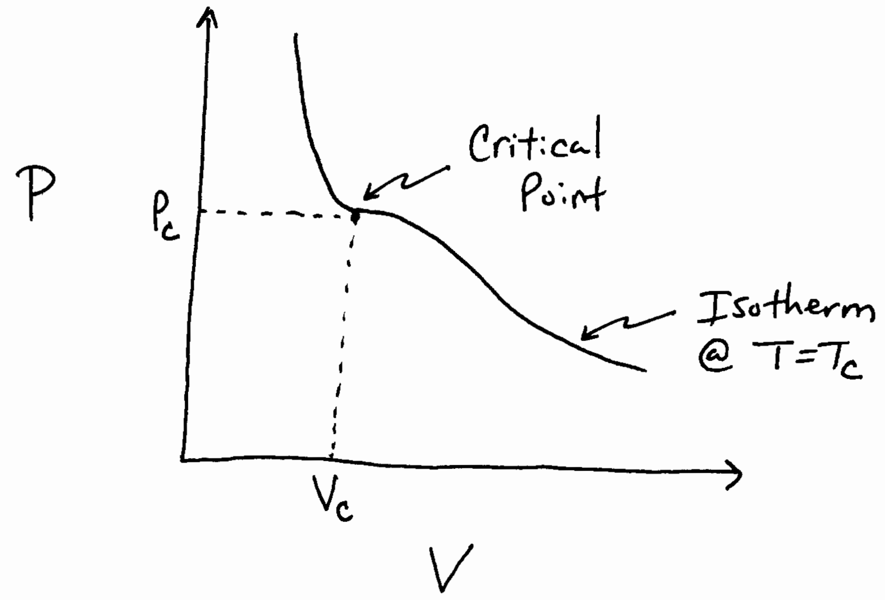
How do I get these parameters?

Determination of Equation of State Parameters

Option 1: Fit equation to PVT data

Option 2: Estimate from T_c + P_c

⇒ Look at T_c isotherm...



At Critical Point:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad (\text{Slope} = 0)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (\text{Inflection Point})$$

DEMONSTRATE FOR VAN DER WAALS EQUATION...

At critical point, all three roots $= V_c$

$$\Rightarrow \quad (V - V_c)^3 = 0$$

$$\boxed{V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0}$$

Back to Van der Waals, for $P = P_c$ + $T = T_c$

$$P_c = \frac{RT_c}{V-b} - \frac{a}{V^2}$$

Get common denominator and cross-multiply...

$$P_c = \frac{RT_cV^2 - a(V-b)}{(V-b)V^2}$$

$$P_c(V-b)(V^2) = RT_cV^2 - a(V-b)$$

$$V^3 - bV^2 = \frac{RT_c}{P_c}V^2 - \frac{a}{P_c}V + \frac{ab}{P_c}$$

$$\boxed{V^3 + \left(-b - \frac{RT_c}{P_c}\right)V^2 + \left(\frac{a}{P_c}\right)V - \frac{ab}{P_c} = 0}$$

Compare coefficients:

$$\underline{V^3:} \qquad 1 = 1$$

$$\underline{V^2:} \qquad \left(-b - \frac{RT_c}{P_c}\right) = -3V_c \quad \Rightarrow b = 3V_c - \frac{RT_c}{P_c}$$

$$\underline{V:} \qquad \frac{a}{P_c} = 3V_c^2 \quad \Rightarrow \boxed{a = 3P_c V_c^2}$$

$$\underline{V^0:} \qquad -\frac{ab}{P_c} = -V_c^3$$

$$\Rightarrow \frac{(3\cancel{P_c}V_c^2)}{\cancel{P_c}} b = V_c^3$$

$$\Rightarrow \boxed{b = \frac{1}{3} V_c}$$

$$\frac{V_c}{3} = 3V_c - \frac{RT}{P_c} \quad \Rightarrow \frac{8}{3} V_c = \frac{RT_c}{P_c}$$

$$\Rightarrow \boxed{V_c = \frac{3}{8} \frac{RT_c}{P_c}}$$

Therefore:

$$b = \frac{1}{8}\frac{RT_c}{P_c} \qquad a = \frac{27}{64}\frac{R^2 T_c^2}{P_c}$$

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{3}{8} \quad \text{(Van der Waals)}$$

SEE TABLE 3.1.

If we apply to Generic Cubic...

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

or if $T \neq T_c$

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

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

⇒ Redlich/Kwong EOS

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

where

$$\alpha(T_r) = T_r^{-1/2}$$

THEOREM OF CORRESPONDING STATES

(ACENTRIC FACTOR)

$$Z_{\text{FLUID 1}} \approx Z_{\text{FLUID 2}} \quad \text{for same } T_r + P_r$$

where

$$T_r \equiv \frac{T}{T_c} \qquad \text{Reduced Temperature}$$

$$P_r \equiv \frac{P}{P_c} \qquad \text{Reduced Pressure}$$

EOS LIKE VAN DER WAALS + REDLICH/KWONG ARE BASED ON $\underline{\underline{2}}$ PARAMETERS. (T_r + P_r)

WE CAN IMPROVE EOS BY ADDING $\underline{\underline{\text{3RD}}}$ PARAMETER

⇒ ACENTRIC FACTOR, ω

⇒ "ALL FLUIDS HAVING THE SAME VALUE OF ω, WHEN COMPARED AT THE SAME T_r + P_r, HAVE ABOUT THE SAME VALUE OF Z, AND ALL DEVIATE FROM IDEAL-GAS BEHAVIOR TO ABOUT THE SAME DEGREE."

ROOTS OF GENERIC CUBIC EQUATIONS OF STATE:

VAPOR & VAPOR LIKE:

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

OR

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

where $\beta = \Omega \dfrac{P_r}{T_r}$ and $q = \Psi \dfrac{\alpha(T_r)}{\Omega T_r}$

LIQUID & LIQUID LIKE:

$$V = b + (V+\epsilon b)(V+\sigma b)\left[\frac{RT + bP - VP}{a(T)}\right]$$

OR

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

Then $V = \dfrac{ZRT}{P}$

TABLE 3.1

Table 3.1: Parameter Assignments for Equations of State

For use with Eqs. (3.49) through (3.56)

Eq. of State	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	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)	$\alpha_{\mathrm{SRK}}(T_r;\omega)^\dagger$	1	0	0.08664	0.42748	1/3
PR (1976)	$\alpha_{\mathrm{PR}}(T_r;\omega)^\ddagger$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740

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

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

How to choose?

Van der Waals
- → Simple
- → Only 2 parameters

Redlich/Kwong
- → Simple
- → Only 2 parameters
- → $a = f(T)$

Soave/Redlich/Kwong (SRK)
- → Developed for VLE
- → 3 parameters
- → $a = f(T)$

Peng-Robinson
- → Developed for VLE
- → 3 parameters
- → $a = f(T)$
- → More accurate than SRK

EXAMPLE 3.9 Given that the vapor pressure of n-butane @ 350K is 9.4573 bar, find the molar volumes of (a) saturated vapor and (b) saturated liquid n-butane at these conditions as given by the Redlich/Kwong equation.

FROM APPENDIX B:

$T_c = 425.1$ K

$P_c = 37.96$ bar

$$\Rightarrow T_r = \frac{T}{T_c} = 0.8233 \qquad P_r = \frac{P}{P_c} = 0.2491$$

Procedure: Determine Z

Then $V = \dfrac{ZRT}{P}$

To get Z:

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

From Table 3.1:

$\Omega = 0.08664$

$\Psi = 0.42748$

$$\alpha(T_r) = T_r^{-1/2}$$

Next, Plug + Chug.

$$\alpha(T_r) = (0.8233)^{-1/2} = 1.1021$$

$$\beta = 0.08664\left(\frac{0.2491}{0.8233}\right) = 0.02621$$

$$q = \frac{0.42748}{0.08664} \Big/ \frac{1.1021}{0.8233} = 6.6048$$

Next, ~~VAPO~~ VAPOR ROOT

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

Redlich/Kwong: $\epsilon = 0$, $\sigma = 1$

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

$$Z = 1.02621 - \frac{(6.6048)(0.02621)(z-0.02621)}{z\,(z+0.02621)}$$

FROM SOLVER:

$Z = 0.8305$ (Initial Guess: $Z=1$)

$$\Rightarrow V = \frac{ZRT}{P} = \frac{0.8305}{9.4573\,\text{bar}} \left| \frac{83.14\,\text{cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}} \right| 350\,\text{K}$$

$$\boxed{V = 2{,}555\,\frac{\text{cm}^3}{\text{mol}}} \leftarrow \text{GAS PHASE.}$$

NEXT, LIQUID ROOT

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

$$Z = 0.02621 + (Z)(Z + 0.02621)\left(\frac{1.02621 - Z}{(6.6048)(0.02621)}\right)$$

FROM SOLVER:

$Z = 0.0433$ (Initial Guess: $Z = \beta$)

$$\Rightarrow V = \frac{0.0433}{9.4573\,\text{bar}} \left| \frac{83.14\,\text{cm}^3\,\text{bar}}{\text{mol} \cdot \text{K}} \right| 350\,\text{K}$$

$$\Rightarrow \boxed{V = 133.3\,\frac{\text{cm}^3}{\text{mol}}} \leftarrow \text{LIQ. PHASE}$$

1 EOS GIVES VAPOR + LIQUID DENSITY.

⇒ BIG IMPROVEMENT SINCE IDEAL GAS LAW.

Results for other EOS:

For comparison, values of V^v and V^l calculated for the conditions of Ex. 3.9 by all four of the cubic equations of state considered here are summarized as follows:

V^v/cm^3 mol^{-1}					V^l/cm^3 mol^{-1}				
Exp.	vdW	RK	SRK	PR	Exp.	vdW	RK	SRK	PR
2,482	2,667	2,555	2,520	2,486	115.0	191.0	133.3	127.8	112.6

3.6 GENERALIZED CORRELATIONS FOR GASES

→ Popular

→ Z, B, C from critical + reduced properties.

Pitzer Correlations for Compressibility Factor

$$Z = Z^0 + \omega Z'$$

$$Z^0, Z' = f(P_r, T_r)$$

T_c, P_c, V_c, ω in Appendix B.

Most popular: Lee/Kesler

Values for Z^0 + Z' in Appendix E.

- GREAT FOR NON-POLAR OR SLIGHTLY POLAR GASES
- POLAR GASES OR GASES THAT ASSOCIATE (MORE INTERACTIONS) ⇒ MORE ERROR

Very Simple Gases? (H2, He, Ne) Does not work directly. Need *effective* critical parameters:

$$T_c\,(K) = \frac{43.6}{1 + \frac{21.8}{2.016\,T}} \quad (\text{for } H_2)$$

$$P_c\,(\text{bar}) = \frac{20.5}{1 + \frac{44.2}{2.016\,T}} \quad (\text{for } H_2)$$

$$V_c\left(\frac{\text{cm}^3}{\text{mol}}\right) = \frac{51.5}{1 - \frac{9.91}{2.016\,T}} \quad (\text{for } H_2)$$

$$\omega = 0$$

Why show for H_2? Most commonly found gas in chemical processing.

Pitzer Correlations for the Second Virial Coefficient.

$$Z = 1 + B^{\circ} \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$$

$$\Rightarrow Z^{\circ} = 1 + B^{\circ} \frac{P_r}{T_r}$$

$$Z' = B' \frac{P_r}{T_r}$$

where;

$$B^{\circ} = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Correlations for the Third Virial Coefficient

See Smith & Van Ness

pp. 103 - 104.

EXAMPLE 3.10 Determine the molar volume of n-butane at 510 K and 25 bar by each of the following:

(a) The ideal gas law.

(b) The generalized compressibility factor correlation.

(c) Equation (3.61), with the generalized correlation for $\hat{B}$.

(d) Equation (3.68), with the generalized correlations for $\hat{B}$ and $\hat{C}$.

(a) Ideal Gas Law.

$$V = \frac{RT}{P} = \frac{83.14 \text{ cm}^3 \cdot \text{bar}}{\text{mol} \cdot \text{K}} \left| \frac{510 \text{ K}}{25 \text{ bar}} \right. = \boxed{1,696.1 \frac{\text{cm}^3}{\text{mol}} = V}$$

(b) $Z = Z^\circ + \omega Z'$

FROM APPENDIX B: (for n-butane)

$\omega = 0.200$

$T_c = 425.1 \text{ K}$

$P_c = 37.96 \text{ bar}$

Next, $T_r = \dfrac{510}{425.1} = 1.200$

$$P_r = \frac{25}{37.96} = 0.659$$

Then, to Appendix E,

from Table E.1

T_r	$P_r = 0.6000$	$P_r = 0.8000$
1.200	$Z^\circ = 0.8779$	$Z^\circ = 0.8330$

Linear interpolation:

$$\frac{0.659 - 0.600}{0.800 - 0.600} = \frac{Z^\circ - 0.8779}{0.8330 - 0.8779}$$

$$\Rightarrow \boxed{Z^\circ = 0.8647}$$

from Table E.2

T_r	$P_r = 0.600$	$P_r = 0.800$
1.200	$Z' = 0.0326$	$Z' = 0.0499$

Linear interpolation: →

$$\frac{0.659-0.600}{0.800-0.600} = \frac{z'-0.0326}{0.0499-0.0326}$$

$$\Rightarrow \boxed{Z' = 0.0377}$$

$$\Rightarrow Z = 0.8647 + (0.200)(0.0377)$$

$$\boxed{Z = 0.8722}$$

$$V = \frac{ZRT}{P} = \frac{0.8722}{25\ \text{bar}} \left| \frac{83.14\ \text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}} \right| \frac{510\ \text{K}}{1}$$

$$\boxed{V = 1{,}479.3\ \frac{\text{cm}^3}{\text{mol}}}$$

(c) $$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\frac{P_r}{T_r}$$

where $$\hat{B} = \frac{BP_c}{RT_c}$$

$$B^{\circ} = 0.083 - \frac{0.422}{(1.200)^{1.6}} = -0.2322$$

$$B' = 0.139 - \frac{0.172}{(1.200)^{4.2}} = 0.0590$$

$$\hat{B} = -0.2322 + (0.200)(0.0590) = -0.2204$$

$$\Rightarrow Z = 1 + (-0.2204)\frac{0.659}{1.200} = 0.8790$$

$$\Rightarrow V = \frac{0.8790}{25\text{ bar}} \bigg| \frac{83.14\text{ cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}} \bigg| \frac{510\text{ K}}{1}$$

$$\boxed{V = 1{,}490.8\ \frac{\text{cm}^3}{\text{mol}}}$$

(d) Need $\hat{C}$

$$\hat{C} = C^{\circ} + \omega C'$$

$$C^{\circ} = 0.01407 + \frac{0.02432}{1.200} - \frac{0.00313}{(1.200)^{10.5}}$$

$$\boxed{C^{\circ} = 0.0340}$$

$$C' = -0.02676 + \frac{0.05539}{(1.200)^{2.7}} - \frac{0.00242}{(1.200)^{10.5}}$$

$$\boxed{C' = 0.00674}$$

$$\hat{C} = 0.0340 + (0.200)(0.00674)$$

$$\boxed{\hat{C} = 0.0353}$$

$$Z = 1 + \hat{B}\frac{P_r}{T_r Z} + \hat{C}\left(\frac{P_r}{T_r Z}\right)^2$$

$$Z = 1 + \frac{(-0.2204)(0.659)}{(1.200)Z} + (0.0353)\left[\frac{(0.659)}{(1.200)Z}\right]^2$$

$$Z = 1 - \frac{0.1210}{Z} + \frac{0.0106}{Z^2}$$

SOLVER: (Initial Guess $Z=1$)

$$\boxed{Z = 0.8756}$$

$$V = \frac{0.8756}{25\ \text{bar}} \left| \frac{83.14\ \text{cm}^3\cdot\text{bar}}{\text{mol}\cdot\text{K}} \right| \frac{510\ \text{K}}{1} = \boxed{1{,}485.1\ \frac{\text{cm}^3}{\text{mol}} = V}$$

EXAMPLE 3.11 What pressure is generated when 1 lbmol of methane is stored in a volume of 2 ft³ at 122 °F? Base calculations on each of the following:

(a) Ideal Gas Law

(b) The Redlich/Kwong equation.

(c) A generalized correlation.

(a) Ideal Gas Law

$$P = \frac{nRT}{V^t} = \frac{0.7302\ \cancel{ft^3}\cdot atm}{lbmol \cdot \cancel{R}} \left| \frac{(122+459.67)\cancel{R}}{2\ \cancel{ft^3}} \right| \frac{1\ lbmol}{1}$$

$$\boxed{P = 212.4\ atm}$$

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

w/ $\alpha(T_r) = T_r^{-1/2}$

⇒ Need critical values (Appendix B).

for methane ...

$$\omega = 0.012 \qquad T_c\,(K) = 190.6\,K = 343.1\,R$$

$$P_c = 45.99 \text{ bar} = 45.39 \text{ atm}$$

$$\Rightarrow T_r = \frac{(122 + 459.67)}{343.1} = 1.695$$

Next, $a(T) = \Psi \dfrac{\alpha(T_r) R^2 T_c^2}{P_c}$

$$b = \Omega \frac{R T_c}{P_c}$$

$$\alpha(1.695) = (1.695)^{-1/2} = 0.7681$$

$$\left.\begin{aligned} \Psi &= 0.42748 \\ \Omega &= 0.08664 \end{aligned}\right\} \text{ from Table 3.1}$$

$$a(T) = \frac{(0.42748)(0.7681)}{45.39 \text{ atm}} \left| \frac{(0.7302)^2 \, ft^6 atm^2}{lbmol^2 \cdot R^2} \right| \frac{(343.1\,R)^2}{1}$$

$$\boxed{a(T) = 454.0 \ \frac{atm \cdot ft^6}{lbmol^2}}$$

$$b = \frac{0.08664}{45.39\ \text{atm}} \bigg| \frac{0.7302\ \text{ft}^3\cdot\text{atm}}{\text{lbmol}\cdot\text{R}} \bigg| \frac{343.1\ \text{R}}{1}$$

$$\boxed{b = 0.478\ \frac{\text{ft}^3}{\text{lbmol}}}$$

$$V = \frac{2\ \text{ft}^3}{1\ \text{lbmol}} = 2\ \frac{\text{ft}^3}{\text{lbmol}}$$

Plug + Chug

$$P = \frac{0.7302\ \text{ft}^3\cdot\text{atm}}{\text{lbmol}\cdot\text{R}} \bigg| \frac{(122+459.67)\text{R}\cdot\text{lbmol}}{(2-0.478)\ \text{ft}^3}$$

$$- \frac{454.0\ \text{atm}\cdot\text{ft}^6}{\text{lbmol}^2} \bigg| \frac{\text{lbmol}}{2\ \text{ft}^3} \bigg| \frac{\text{lbmol}}{(2+0.478)\ \text{ft}^3}$$

$$\boxed{P = 187.46\ \text{atm}}$$ (<u>big difference</u>)

(c) Need P_r

But $P_r = \frac{P}{P_c}$ ← unknown ⇒ Iterative method.

$$P = \frac{ZRT}{V} = \frac{Z\,(0.7302\ ft^3\cdot atm)}{lbmol\cdot R}\bigg|\frac{(122+459.67)R\cdot lbmol}{2\ ft^3}$$

$$P = 212.4\ Z\ \ (atm)$$

Put in terms of P_r $(P = P_r P_c)$

$$P_r\,(45.39\ atm) = 212.4\ Z\ (atm)$$

$$\boxed{P_r = 4.68\ Z}$$

Now, iteration... $Z = Z^\circ + \omega Z'$

		Interpolation		
Guess Z	P_r	Z°	Z'	New Z
1	4.68	0.8956	0.2711	0.8989
0.8989	4.21	0.8915	0.2597	0.8946
0.8946	4.19	0.8913	0.2592	0.8944

Not much change... $Z = 0.8944$

$$P = \frac{ZRT}{V} = \frac{0.8944\cdot lbmol}{2\ ft^3}\bigg|\frac{0.7302\ ft^3\cdot atm}{lbmol\cdot R}\bigg|\frac{(122+459.67)R}{1}$$

$$\boxed{P = 189.9\ atm}$$

$\boxed{3.7}$ GENERALIZED CORRELATIONS FOR LIQUIDS.

- → CUBIC EOS
  - → USUALLY NOT VERY ACCURATE
- → LEE/KESLER CORRELATION
  - → WORKS WELL
  - → ONLY FOR NON-POLAR OR SLIGHTLY POLAR FLUIDS
- → RACKETT EQUATION
  - → SATURATED LIQUIDS

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}}$$

$$\underline{\underline{\text{or}}}$$

$$Z^{sat} = \frac{P_r}{T_r} Z_c^{\left[1+(1-T_r)^{2/7}\right]}$$

Critical Constants in Appendix B.

→ Two-Parameter Corresponding States

$$\underbrace{\rho_r \equiv \frac{\rho}{\rho_c}}_{\text{Densities}} = \frac{V_c}{V}$$

→ Use Fig. 3.16 to get V.

→ <u>OR</u>

$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}}$$

where V_1 = known ; ρ_{r_1} + ρ_{r_2} from Fig. 3.16.

FIGURE 3.16

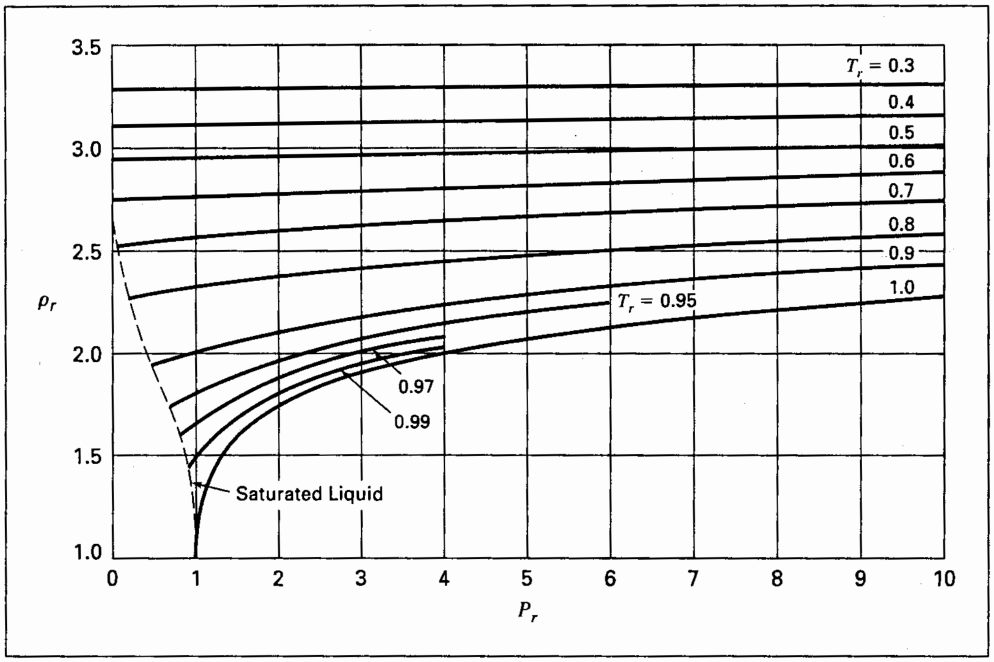


Figure 3.16: Generalized density correlation for liquids.

EXAMPLE 3.13 For ammonia at 310 K, estimate the density of:

(a) The saturated liquid

(b) The liquid at 100 bar.

Critical Properties from Table B.1:

$\omega = 0.253$

$T_c(K) = 405.7\,K$ $\Rightarrow T_r = \frac{310\,K}{405.7\,K}$

$P_c(bar) = 112.80\,bar$

$T_r = 0.764$

$Z_c = 0.242$

$V_c = 72.5\,\frac{cm^3}{mol}$

(a) Rackett Equation

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}} = \left(72.5\,\frac{cm^3}{mol}\right)(0.242)^{(1-0.764)^{2/7}}$$

$$\boxed{V^{sat} = 28.34\,\frac{cm^3}{mol}}$$

(b) Need P_r & ρ_r

$$P_r = \frac{100\,bar}{112.80\,bar} = 0.887$$

FROM FIG. 3.16,

$\rho_r \approx 2.4$

$$\Rightarrow V = \frac{V_c}{\rho_r} = \frac{72.5\,\text{cm}^3}{\text{mol}}\left|\frac{1}{2.4}\right. = \boxed{30.21\ \frac{\text{cm}^3}{\text{mol}} = V},$$

⇒ LOTS OF ERROR INTRODUCED READING FIG. 3.16.

Experimental value for $V^{sat} = 29.14\ \frac{\text{cm}^3}{\text{mol}}$

⇒ Rackett Equation is pretty good.

Coupled with approximate incompressibility of liquids, Rackett Equation often used to approximate V too.

Next: Chapter 4 – Heat Effects.