


Welcome to Fuga-city!

An intro to  Thermodynamics, as taught by a bunch of chemical engineering juniors-to-be

This name will make sense later, don't worry

Let's get started with a few key bits

What is a Fluid?

 fluid

/'flʊɪd/ noun

a substance that has no fixed shape and yields easily to external pressure



In this class we'll use SI units, the international standard for units

V, Volume: a measurement of space

L, mL, m³, cm³, gal
← SI units

P, Pressure: force over an area

$$\frac{F}{A} \rightarrow \frac{N}{m^2} \rightarrow \frac{kg \cdot m/s^2}{m^2} \rightarrow Pa \quad \leftarrow \text{SI units}$$

Atm P = 101,325 Pa
101.325 kPa

T, Temperature: at the molecular level, the average kinetic energy of those molecules

°C, K ← K °C + 273.15

↑ 0°C water freeze
100°C water boil

0 K is absolute zero

Gas Time!

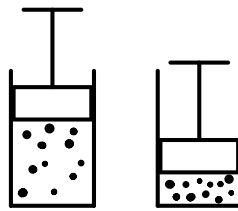
Let's look at these dudes



Robert Boyle (Bobby)

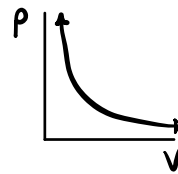


Edme Mariotte



Squishing some gas, what will it do?

Math Part



when you hold all else constant, P goes up as V goes down, and vice versa

$$P \propto \frac{1}{V}$$

↑ "is proportional to"

Pressure and Volume was their jam

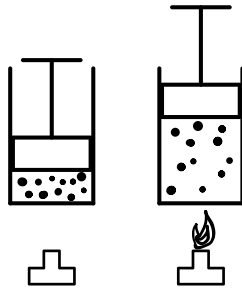
Boyle-Mariotte Law

More dudes

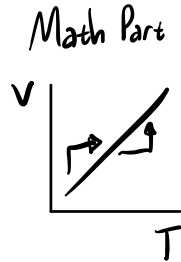


Jacques Charles
getting funky with Volume
and Temperature

Charles' Law



Heating some gas,
what will it do?



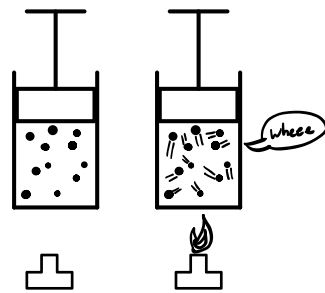
when you hold all else constant
V increases with T
 $V \propto T$

only a few more dudes now

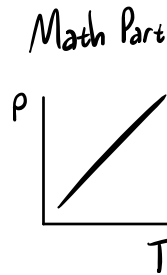


Joseph Louis Gay-Lussac
Pressure and Temperature

Gay-Lussac's Law



Heating some gas,
what will it do?



when you hold all
else constant,
P increases with T
 $P \propto T$

Ok last(ish) ones



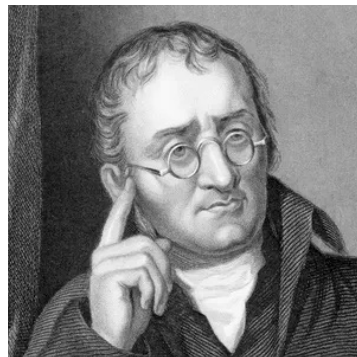
Amedeo Avogadro

Two equal volumes of gas
have the same number
of molecules, even if the
gases are different.
(approximately)

1 mole of any gas at STP
occupies 22.4 L ρ_{oc}
(STP = 101.325 kPa, 273.15 K)
Standard Temperature and Pressure

$1 \text{ mole} = 6.022 \times 10^{23}$ 602200000000000000000000

Dalton's Law of Partial Pressures



John Dalton

↳ Things... they add up

$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$

$\begin{matrix} \downarrow P_2 & \downarrow P_1 & \downarrow P_3 \\ \dots P_4 + P_5 + P_6 + \\ \dots P_7 + P_8 + P_9 + \\ \dots P_{10} + P_{11} + P_{12} + \\ \dots P_{13} + P_{14} + P_{15} + \\ \dots P_{16} + P_{17} + P_{18} + \\ \dots P_{19} + P_{20} + P_{21} + \\ \dots P_{22} + P_{23} + P_{24} + \\ \dots P_{25} + P_{26} + P_{27} + \\ \dots P_{28} + P_{29} + P_{30} + \\ \dots P_{31} + P_{32} + P_{33} + \\ \dots P_{34} + P_{35} + P_{36} + \\ \dots P_{37} + P_{38} + P_{39} + \end{matrix}$

Bringing it all together!

What is an ideal gas?

- made of particles that...
- experience no intermolecular forces
- have no size

← smaller than this



Benoit Paul
Émile Clapeyron



IMAGE NOT AVAILABLE

August
Krönig



Rudolf
Clausius

you'll
hate them
later

Ideal Gas Law

ideal gas constant

$$PV = nRT \text{ or } Pv = RT$$

← # moles ← units of energy

where $v = \frac{V}{n}$ ← moles ← units: $\frac{m^3}{mol}$

↑ molar volume

$$R = 8.3145 \frac{J}{mol \cdot K} \rightarrow \frac{kg \cdot m^2/s^2}{mol \cdot K}$$

$$R = \frac{Pv}{T} \leftarrow \text{constant for an ideal gas}$$

$$P = \frac{RT}{v} \text{ Boyle -Mariotte } (P \propto \frac{1}{v}), \text{ constant } T$$

$$v = \frac{RT}{P} \text{ Charles } (v \propto T), \text{ constant } P$$

$$P = \frac{RT}{v} \text{ Gay-Lussac } (P \propto T) \text{ constant } v$$

Example time

$$v = 69 \text{ m}^3/mol$$

$$T = 420 \text{ K}$$

$$Pv = RT$$

$$P = \frac{RT}{v}$$

$$P = \frac{(8.3145 \text{ J/K} \cdot \text{mol})(420 \text{ K})}{69 \text{ m}^3/mol} = 50.61 \text{ Pa}$$

$$P = 69420 \text{ Pa}$$

$$v = 749 \text{ m}^3$$

$$Pv = RT$$

$$T = \frac{Pv}{R}$$

$$T = \frac{(69420 \text{ Pa})(749 \text{ m}^3/mol)}{8.3145 \text{ J/K} \cdot \text{mol}} = 6.253 \times 10^6 \text{ K}$$

these numbers were
chosen by the students

Whoa there friend → **Chemistry and Math**
Background Time

Behold, an atom

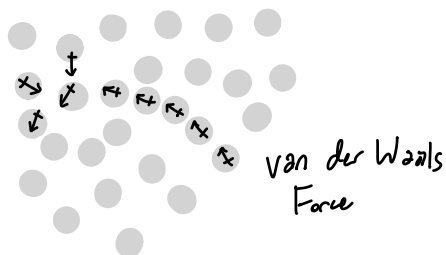
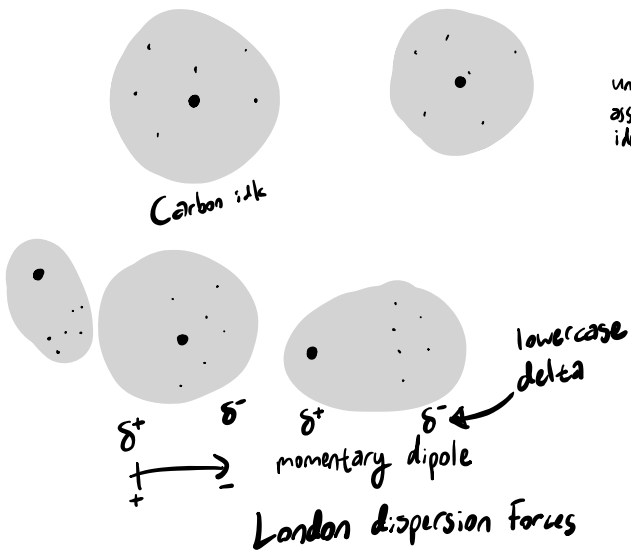


models of atoms
 negatively charged electrons
 nucleus with positively charged protons and neutral neutrons (no charge)
 Jimmy Neutron thing (not accurate)



mostly empty space, but they still take up space

unlike what we assumed for an ideal gas



for example, $\Delta x = x_2 - x_1$
 final value ← initial value
 Δ delta, used to indicate large differences (Δ) or small differences (δ)

α alpha
 $\neq \propto$ proportional

β beta
 Γ, γ gamma

θ theta

ξ ksi

Σ, σ sigma
 $\Sigma_i^n p_i$ "sum from the i th element to the n th element"

ν nu

κ kappa

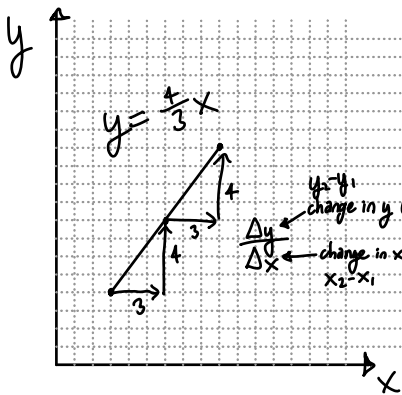
Φ phi

Ω, ω omega

\hbar h-bar
 Planck's constant

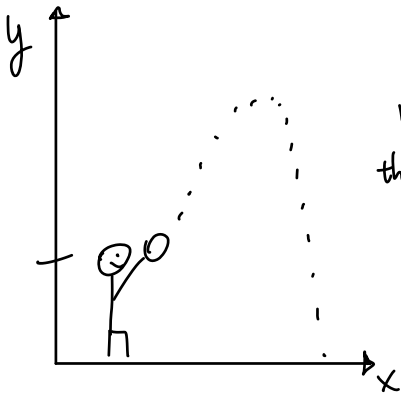
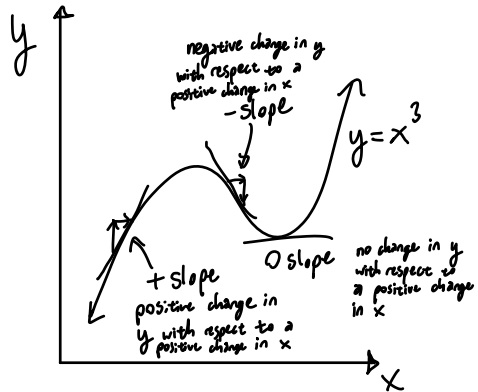
Π, π pi
 (or π if you're into that "I guess")

Now a little bit of calculus slope = rate of change

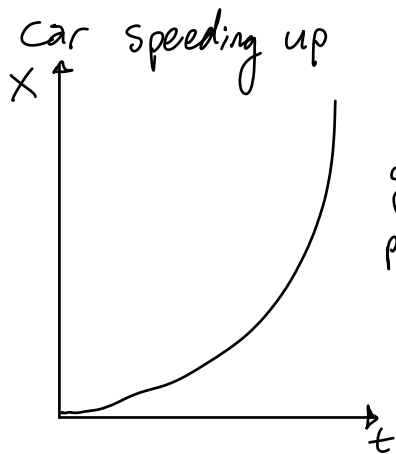


if you've seen this equation for a line before: $y = mx + b$, m is referring to the slope of the line, the rate of change of that line.

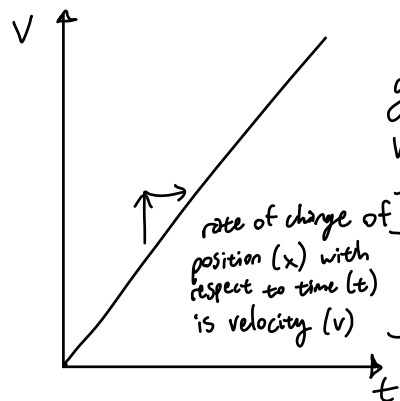
How much is one variable changing with respect to the other?
 y changes by $+4$ when x changes by $+3$



What about...
 the rate of change of...
 the rate of change?



graph of position vs. time

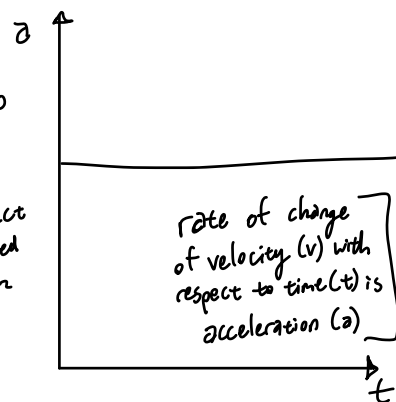


graph of velocity vs. time

$$\left[\begin{array}{l} \text{derivative of } x \text{ with respect to } t \text{ is } v \\ \text{is velocity (v)} \end{array} \right] = \left[\begin{array}{l} \text{derivative of } x \text{ with respect to } t \text{ is } v \\ v = \frac{dx}{dt} \end{array} \right]$$

And the calculus bit...

$v = \frac{dx}{dt}$
 opposites
 $x = \int v dt$ or... $h = \int_{T_1}^{T_2} C_p dT$
 antiderivative, integral
 slope, rate of change, derivative
 molar heat capacity at a constant pressure
 $C_p = \left(\frac{\partial h}{\partial T} \right)_p$
 derivative of h with respect to T at a constant p
 molar enthalpy
 integral of C_p with respect to T evaluated from T_1 to T_2

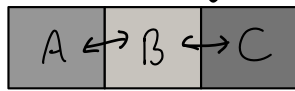


graph of acceleration vs. time

$$\left[\begin{array}{l} \text{rate of change of velocity (v) with respect to time (t) is acceleration (a)} \end{array} \right] = \left[\begin{array}{l} \text{derivative of } v \text{ with respect to } t \text{ is } a \\ a = \frac{dv}{dt} = \frac{d}{dt} \left(\frac{dx}{dt} \right) \end{array} \right]$$

The Laws of Thermodynamics

0th Law:



$$T_A = T_B$$

$$T_B = T_C$$

therefore
 $\therefore T_A = T_C$

1st Law:

$$\Delta U = Q + W$$

change in internal energy
change

(or $dU = \delta Q + \delta W$)

Why is W positive?
 define W as work done on the system by its surroundings
 (work (energy) put in = +W)
 (work (energy) put out = -W)

2nd Law:

$$\Delta S > \frac{\Delta Q}{T_{\text{surroundings}}}$$

or... $dS > \frac{\delta Q}{T}$ entropy of the universe is increasing

3rd Law:

@ 0K $\rightarrow \Delta S = 0$
absolute 0 \rightarrow constant entropy

Properties of things... (lowercase means molar (units/mol))
 that are relevant to thermodynamics

Internal Energy

Entropy (stick around for lessons 5 and 6 to learn more)

$U, u \leftarrow$ units of J, J/mol

$S, s \leftarrow$ units of J/K, $\frac{J}{K \cdot mol}$

relevant equations: $\Delta U = Q + W$
 $\Delta U = T\Delta S - P\Delta V$
 Joules = $J = \frac{kg \cdot m^2}{s^2}$
 the unit of energy

Enthalpy

Gibbs Free Energy

$H, h \leftarrow$ units of J, J/mol
 $H = U + PV$

$G, g \leftarrow$ units of J, J/mol
 $G = H - TS$

relevant equations: $\Delta H = T\Delta S + V\Delta P$

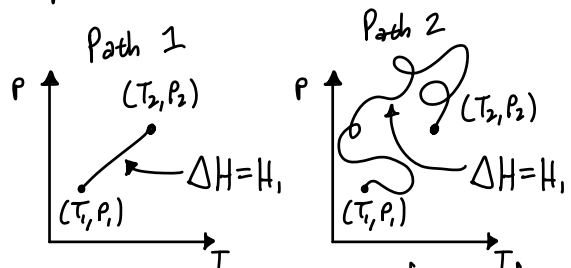
relevant equations: $\Delta G = -\Delta S T + V\Delta P$

Heat Capacity: energy input required to increase temperature by 1 Kelvin

C_v, c_v or C_p, c_p both have units of $\frac{J}{K \cdot mol}$
 $\left(\frac{\partial U}{\partial T}\right)_v \leftarrow$ change in internal energy with respect to temperature at constant volume
 $\left(\frac{\partial H}{\partial T}\right)_p \leftarrow$ change in enthalpy with respect to temperature at constant pressure

What is a State Function?

State functions, or path independent functions, are functions that always give the same value if you start at Point A and end at Point B, no matter how you get there.

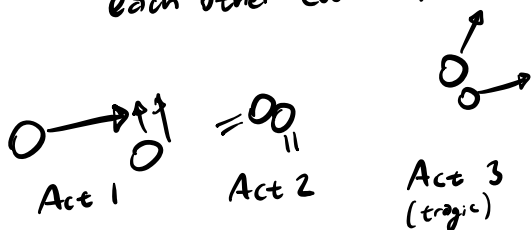


Enthalpy is an example of a state function, ΔH is still the same from (T_1, P_1) to (T_2, P_2)

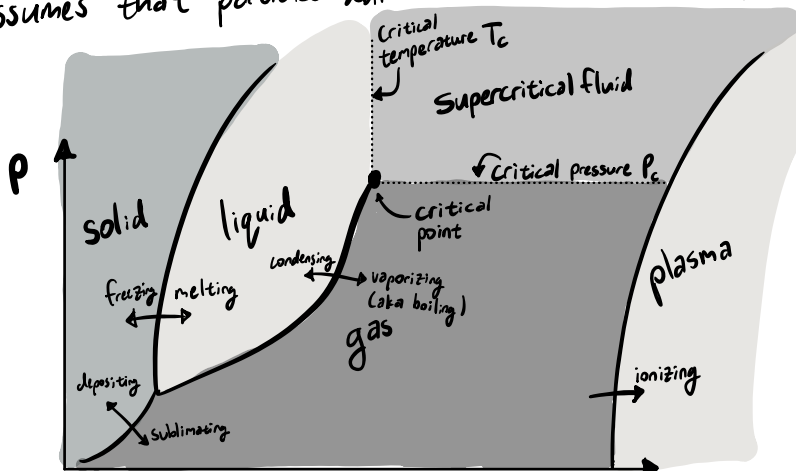
Get Real

get real

What if.. particles have size, and what if they interact with each other (loof ouch)




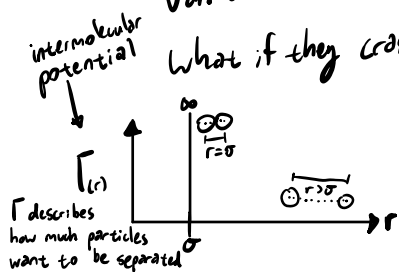
Real matter has... phases! And so the ideal gas law, which assumes that particles don't interact with each other, can't apply to real life.



Phases of matter come about from various intermolecular interactions. At lower temperatures, particles are moving around less, and so come closer together, as they do in the solid state. When they are at higher temperatures, they move around more, as they do in fluid states like liquid and gas.

van der Waals Equation of State (EOS)

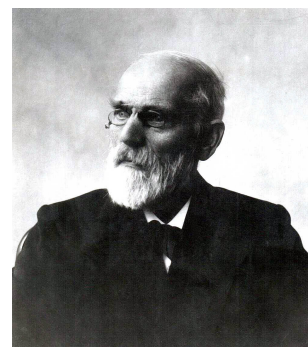
What if they crash into each other, like pool table balls? 



let $\sigma = 2R$ ← radius of particle
 $\sigma = d$ ← diameter of particle

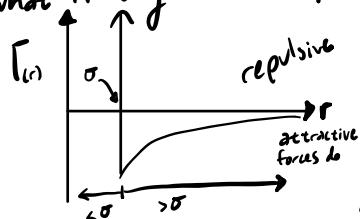
$$Pv = RT \rightarrow P = \frac{RT}{v}$$

let b be a factor that accounts for a particle's size: $P = \frac{RT}{v-b}$



Johannes Diderik van der Waals

what if they attract/repel one another? (Sutherland Model) a good approximation to real fluid behavior



$$\Gamma_{\text{Sutherland}} = \begin{cases} -a/r^2, & r > \sigma \\ \infty, & r \leq \sigma \end{cases}$$

van der Waals (vdW) equation

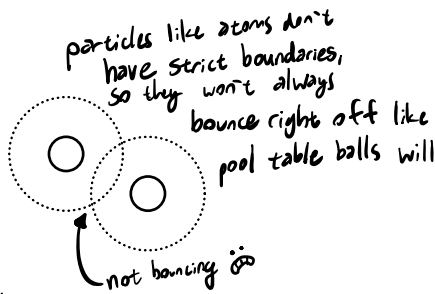
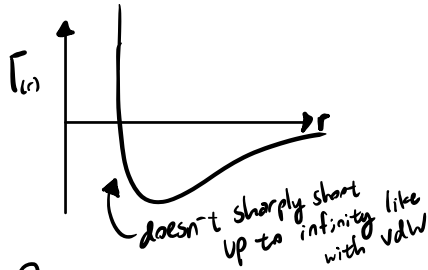
$$P = \frac{RT}{v-b} \rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2}$$

let a be a factor that accounts for attractive/repulsive interactions between particles

About a and b : these are experimentally determined constants that are unique to each gas. You can find a gas's vdW constants in tables or by searching for them online.

But... it's just a model \therefore

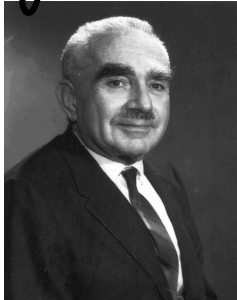
For a real fluid...



Redlich-Kwong EOS:



Joseph Ning Shun Kwong



Otto Redlich

Both were chemical engineers! Go ChemE

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

where $a = \frac{1}{9(\sqrt{2}-1)} \frac{R^2 T_c^{2.5}}{P_c}$, $b = \frac{\sqrt{2}-1}{3} \frac{RT_c}{P_c}$

This model

Critical temperature T_c of the fluid of interest

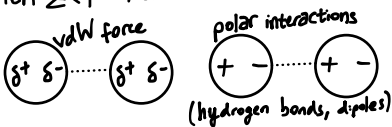
Critical pressure P_c of the fluid of interest

This model to describe the relationship between P , T , and v of a real fluid is quite accurate! This equation, while still only a model to describe the behavior of fluids, does a better job at doing so than the van der Waals equation, and a much better job than the ideal gas law. Also it's simpler in form than other equations of state that are similar in accuracy, like the scary-looking Benedict-Webb-Rubin equation (Google if you dare).

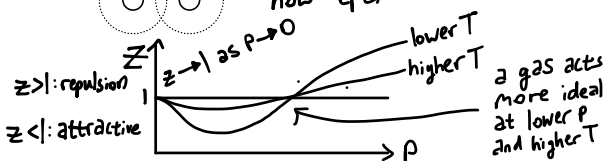
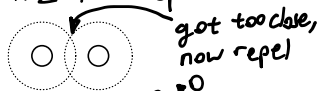
Let's get funky with the compressibility factor, Z

We'll define $Z = \frac{Pv}{RT}$, or $Pv = ZRT$

When $Z < 1$ \rightarrow attractive forces dominate



When $Z > 1$ \rightarrow repulsive forces dominate



Virial Expansion

Writing Z as a power series in terms of P (or $1/v$)

$$Z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + E'P^4 + \dots$$

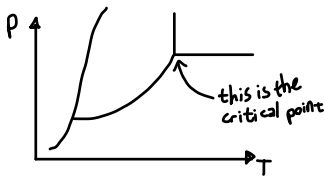
$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \dots$$

where $B(T), B'(T)$ are the second virial coefficients, $C(T), C'(T)$ are the third virial coefficients, and so on.....

Principle of Corresponding States: Fluids act similarly when considered relative to their critical points. This means that when we account for a fluid's critical properties, most fluid will behave nearly the same.

What is a reduced property?

Remember this diagram?



at the critical point, each property (P, V, T) is also at its critical value
we have, for every fluid, a critical temperature (T_c), a critical pressure (P_c), and a critical molar volume (v_c)

When we consider reduced properties, we consider some P, v, or T with their respective critical values divided out.

reduced pressure $P_r = \frac{P}{P_c}$ ← the pressure of the fluid
← the critical pressure of the fluid

reduced temperature $T_r = \frac{T}{T_c}$

reduced volume $v_r = \frac{v}{v_c}$

by this definition, when

$P_r = 1$, then $P = P_c$

$T_r = 1$, then $T = T_c$

$v_r = 1$, then $v = v_c$

these values are all dimensionless, meaning that they have no units, without the context provided by the equations intended, these values can lose their meaning, so be careful!

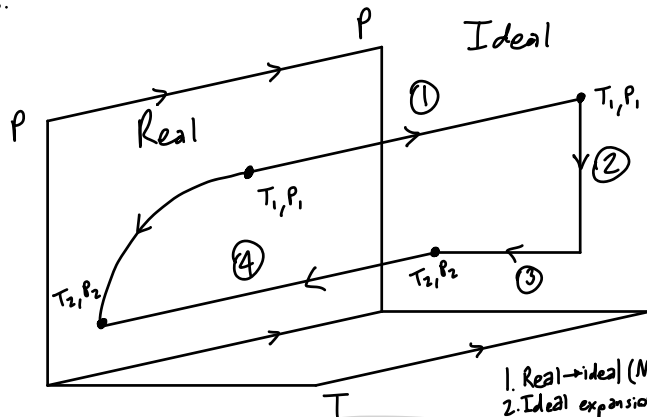
Lee-Kesler: $z = z^{(0)}(T_r, P_r) + \omega z^{(1)}(T_r, P_r)$

This model can be used to approximate (with pretty good accuracy) the behavior of real fluids! To use it, refer to a Lee-Kesler chart that provides values for $z^{(0)}$ and $z^{(1)}$ which are generalized to all fluids by the principle of corresponding states, as well as for the eccentric factor ω , which accounts for molecular differences between fluids. $z^{(0)}$ and $z^{(1)}$ are functions of T_r and P_r (reduced properties), so you can get each value simply by referring to the aforementioned Lee-Kesler charts.

Departure Functions

Let M be some path-independent property of a fluid like H, U, or S. For this kind of property, remember that as long as we go from point A to point B, the final value of ΔM will be the same.

ΔM here is short for $M_2 - M_1$, where we start at some (T_1, P_1) and end at some (T_2, P_2) . It is nontrivial to say that $\Delta M = M_2 - M_1$, because if M was path dependent, this would no longer be true.



1. Real → ideal ($M^{dep}(T_1, P_1)$)
2. Ideal expansion (M_2)
3. Ideal cooling (M_3)
4. Ideal → real (M_4^{dep})

$\Delta M = -M_1^{dep}(T_1, P_1) + \Delta M_2^{ideal} + \Delta M_3^{ideal} + M_4^{dep}(T_2, P_2)$

We define a departure function as a property's departure from, or how much it deviates from, ideality. At different temperatures and pressures, the property may have different values than one might expect from using an ideal gas approximation, but these differences can be quantified using the departure function at the given conditions.

$M^{dep}(T, P) \equiv M^{real}(T, P) - M^{ideal}(T, P)$
"is defined as"

the difference between the real fluid property and the same property for an ideal gas

for molar enthalpy

$h^{dep}(T, P) = \int_0^P (v - T \left(\frac{\partial v}{\partial T}\right)_P) dP$

we can rewrite in terms of reduced properties

$\frac{h^{dep}(T, P)}{RT_c} = -T_r^2 \int_0^{P_r} \frac{1}{P_r} \left(\frac{\partial z}{\partial T_r}\right)_{P_r} dP_r$

for molar entropy

$S^{dep}(T, P) = \int_0^P \left(\frac{R}{P} - \left(\frac{\partial v}{\partial T}\right)_P\right) dP$

which can, in turn, be written in a similar form as the Lee-Kesler model

$\frac{h^{dep}(T, P)}{RT_c} = \left(\frac{h^{dep}(T, P)}{RT_c}\right)^{(0)} + \omega \left(\frac{h^{dep}(T, P)}{RT_c}\right)^{(1)}$