

# 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**  
/'flɔɪd/ 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

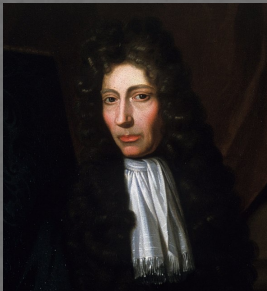
V, Volume: a measurement of space  
L, mL, m<sup>3</sup>, cm<sup>3</sup>, gal  
SI units

P, Pressure: force over an area  
 $\frac{F}{A} \rightarrow \frac{N}{m^2} \rightarrow \frac{kg \cdot m/s^2}{m^2} \rightarrow Pa$  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 K is absolute zero  
0°C water freeze  
100°C water boil

Gas Time!

Let's look at these dudes

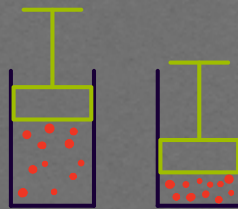


Robert Boyle (Bobby)



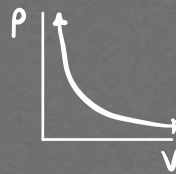
Edme Mariotte

Pressure and Volume was their jam  
Boyle-Mariotte Law



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

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

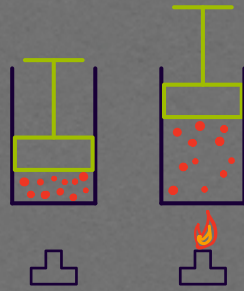
↑ "is proportional to"

More dudes



Jacques Charles  
getting funky with Volume  
and Temperature

### Charles' Law



Heating some gas,  
What will it do?



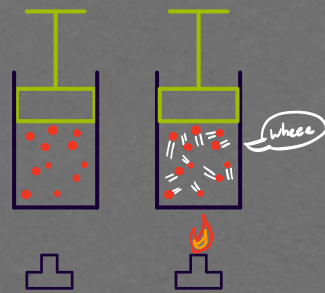
when you hold all else constant  
V increases with T  
 $V \propto T$

only a few more dudes now

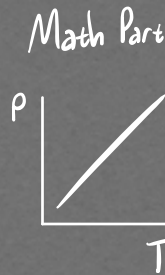


Joseph Louis Gay-Lussac  
Pressure and Temperature

### 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  $\leftarrow$   $\text{m}^3$   
(STP = 101.325 kPa, 273.15 K)  
Standard Temperature and Pressure

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

### Dalton's Law of Partial Pressures



John Dalton

Things... they add up

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots + p_n$$

$\begin{matrix} p_2 & n_2 & p_{\text{CO}_2} \\ \downarrow & \downarrow & \downarrow \end{matrix}$

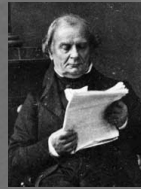
$$\begin{aligned}
 & \dots p_4 + p_5 + p_6 + \\
 & \dots p_7 + p_8 + p_9 + \\
 & \dots p_{10} + p_{11} + p_{12} + \\
 & \dots p_{13} + p_{14} + p_{15} + \\
 & \dots p_{16} + p_{17} + p_{18} + \\
 & \dots p_{19} + p_{20} + p_{21} + \\
 & \dots p_{22} + p_{23} + p_{24} + \\
 & \dots p_{25} + p_{26} + p_{27} + \\
 & \dots p_{28} + p_{29} + p_{30} + \\
 & \dots p_{31} + p_{32} + p_{33} + \\
 & \dots p_{34} + p_{35} + p_{36} + \\
 & \dots p_{37} + p_{38} + p_{39} +
 \end{aligned}$$

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



August  
Krönig



Rudolf  
Clausius

you'll  
have them  
later

## Ideal Gas Law

ideal gas constant

$PV = nRT$  or  $Pv = RT$ , where  $v = \frac{V}{n}$  ← moles ← units:  $\frac{m^3}{mol}$

↑ # moles      ↑ units of energy      ↑ molar volume

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

Hold pink constant

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

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

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

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

## Example time

my iPad cursor kinda sucks

$v = 69 \text{ m}^3/mol$   
 $T = 420 \text{ K}$

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

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

$P = 69420 \text{ Pa}$   
 $v = 749 \text{ m}^3$

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

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

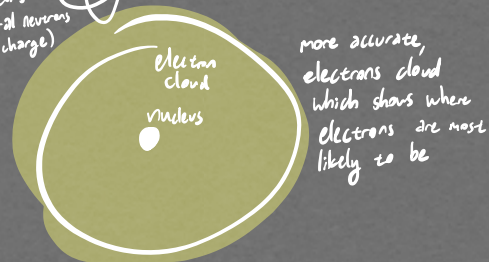
these numbers were  
chosen by the students

# 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

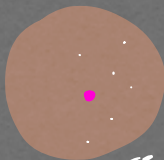
for example,  $\Delta x = x_2 - x_1$   
final value - initial value  
 $\Delta \delta$  delta, used to indicate large differences ( $\Delta$ ) or small differences ( $\delta$ )

$\alpha$  alpha  
 $\propto$  proportional

$\Gamma, \gamma$  gamma



unlike what we assumed for an ideal gas



lowercase delta  
 $\delta^+$   $\delta^-$   $\delta^+$   $\delta^-$   
momentary dipole

London dispersion forces

$\theta$  theta

$\xi$  ksi

$\Sigma, \sigma$  sigma

$\sum_i^n p_i$  "sum from the  $i$ th element to the  $n$ th element"

$\nu$  nu

$\kappa$  kappa

$\Phi$  phi

$\Omega, \omega$  omega

$\Pi, \pi$  pi

$\hbar$  h-bar

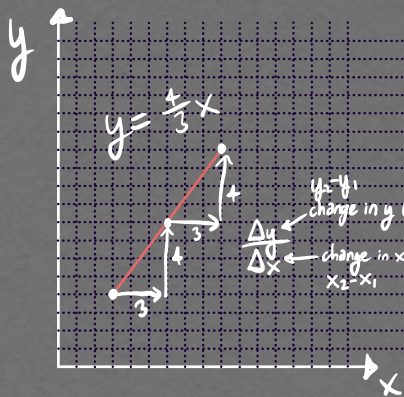
(or  $\pi$  if you're into that I guess)

Planck's constant



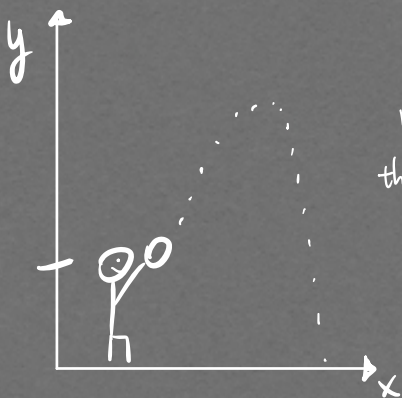
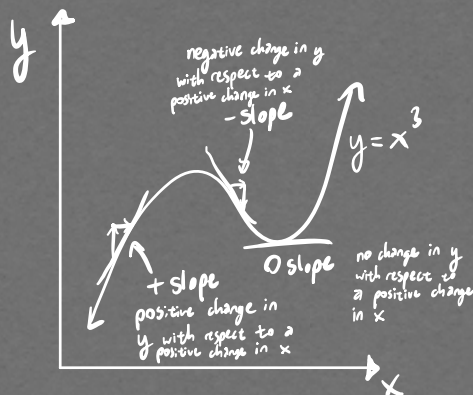
van der Waals Force

# Now a little bit of calculus slope = rate of change



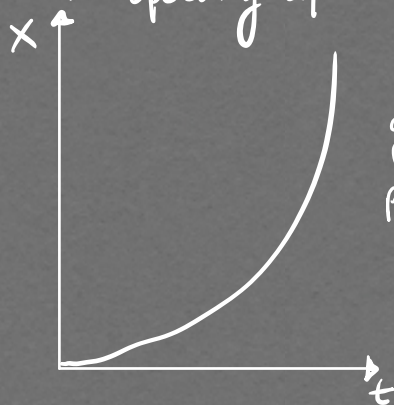
if you've seen this equation for a line before:  $y = mx + b$ ,  $m$  is referring to the **slope** of the line, the rate of change of that line.

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

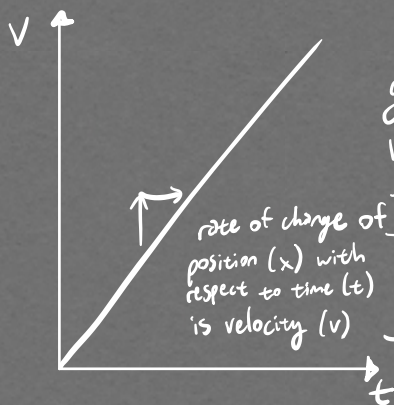


What about...  
 the rate of change of...  
 the rate of change?

car speeding up



graph of position vs. time



graph of velocity vs. time

rate of change of position ( $x$ ) with respect to time ( $t$ ) is velocity ( $v$ )

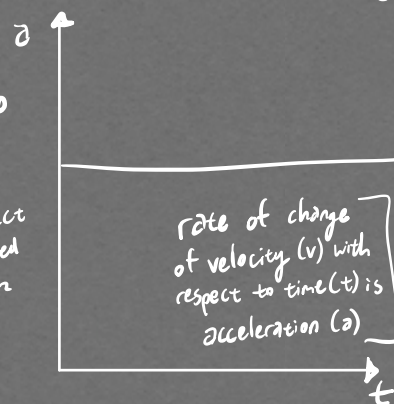
$$= \left[ \begin{array}{l} \text{derivative of } x \text{ with respect to } t \\ \text{is } v \\ v = \frac{dx}{dt} \end{array} \right]$$

and the calculus bit...

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  $p$

$v = \frac{dx}{dt}$   
 slope, rate of change, derivative

opposites ↓  
 $x = \int v dt$  or...  $h = \int_{T_1}^{T_2} C_p dT$  → integral of  $C_p$  with respect to  $T$  evaluated from  $T_1$  to  $T_2$   
 anti-derivative, integral

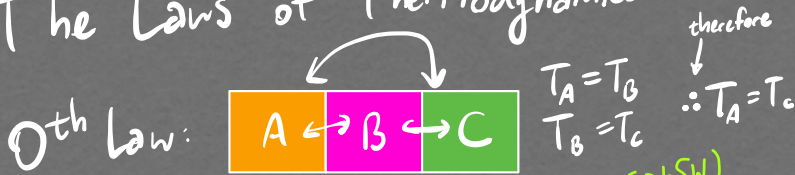


graph of acceleration vs. time

rate of change of velocity ( $v$ ) with respect to time ( $t$ ) is acceleration ( $a$ )

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

# The Laws of Thermodynamics



- 1st Law:  $\Delta U = Q + W$  (change in internal energy = heat + work) (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:  $e \rightarrow 0 \rightarrow \Delta S = 0$  absolute 0 constant entropy

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

Internal Energy  $U, u$  Entropy  $S, s$  (stick around for lessons  $S$  and  $s$  to learn more)

$U, u$  ← units of  $J, J/mol$   $S, s$  ← 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

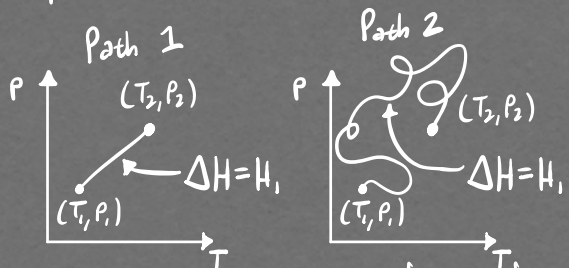
Enthalpy  $H, h$  Gibbs Free Energy  $G, g$   
units of  $J, J/mol$  units of  $J, J/mol$   
relevant equations:  $H = U + PV$   $G = H - TS$   
 $\Delta H = T\Delta S + P\Delta V$  relevant equations:  $\Delta G = -S\Delta T + V\Delta P$

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

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

What is a State Function?

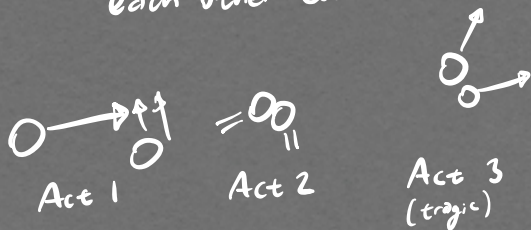
State functions, or path independent functions, are functions that always give the same value if you start at Point A and end at Point B, no matter how you get there.



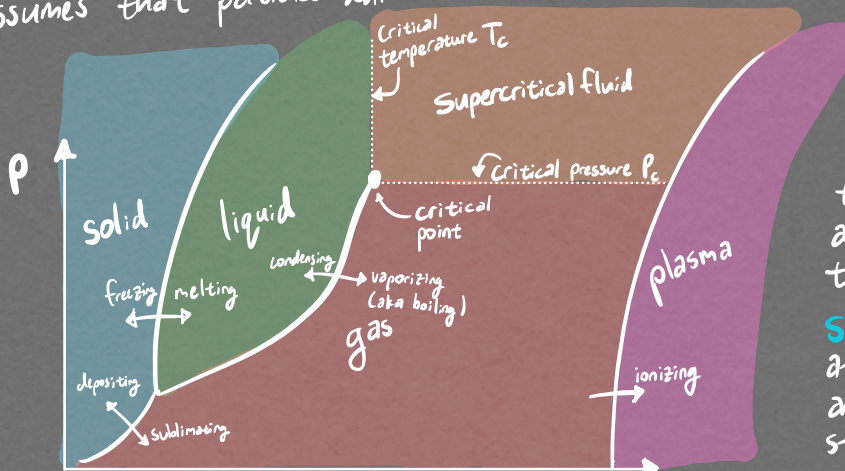
Enthalpy is an example of a state function,  $\Delta H$  is still the same from  $(T_1, P_1)$  to  $(T_2, P_2)$

# Get Real

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



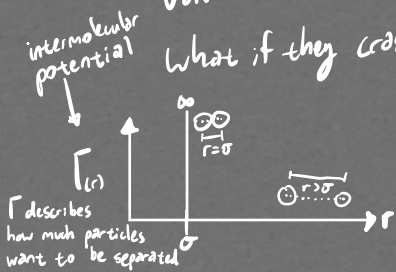
Real matter has... phases! And so the ideal gas law, which assumes that particles don't interact with each other, can't apply to real life.



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**.

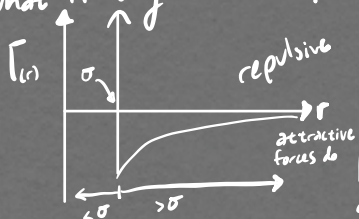
## van der Waals Equation of State (EOS)

What if they crash into each other, like pool table balls? 8



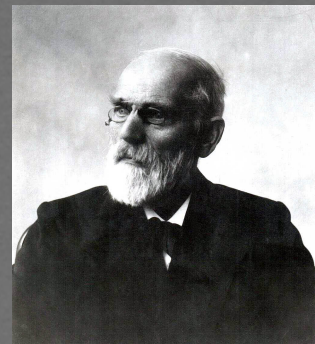
let  $\sigma = 2R$  ← radius of particle  
 $\sigma = d$  ← diameter of particle  
 $PV = RT \rightarrow P = \frac{RT}{V}$   
let  $b$  be a factor that accounts for a particle's size:  $P = \frac{RT}{V-b}$

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



$\Gamma_{\text{sutherland}} = \begin{cases} -a/r^{12}, & r > \sigma \\ \infty, & r \leq \sigma \end{cases}$  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

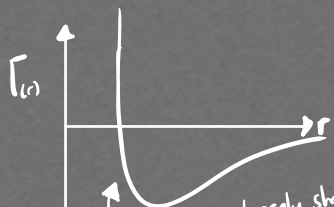


Johannes Diderik van der Waals

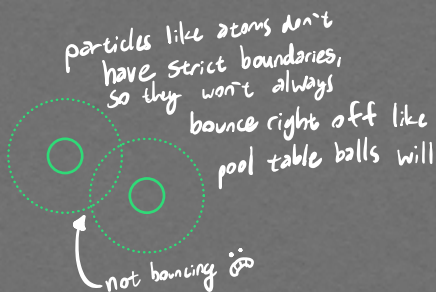
About  $a$  and  $b$ : these are experimentally determined constants that are unique to each gas. You can find a gas's vdW constants in tables or by searching for them online.

But... it's just a model ∴

For a real fluid...



doesn't sharply shoot up to infinity like with vdW



particles like atoms don't have strict boundaries, so they won't always bounce right off like pool table balls will

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

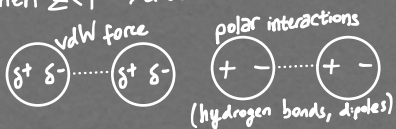
Critical pressure  $P_c$  of the fluid of interest

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 there are similar in accuracy like the scary-looking Benedict-Webb-Rubin equation (google it you dare).

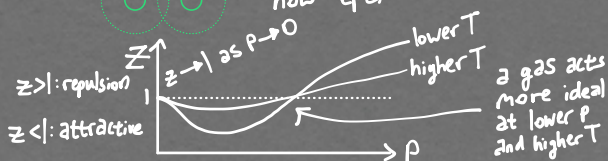
Let's get funky with the compressibility factor,  $z$

We'll define  $z = \frac{Pv}{RT}$ , or  $Pv = zRT$

When  $z < 1$  → attractive forces dominate



When  $z > 1$  → repulsive forces dominate



Virial Expansion

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

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

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

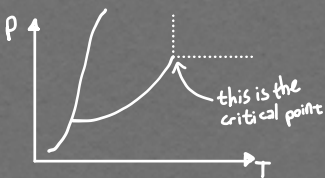
where  $B(T), B'(T)$  are the second virial coefficients,  $C(T), C'(T)$  are the third virial coefficients, and so on.....



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!

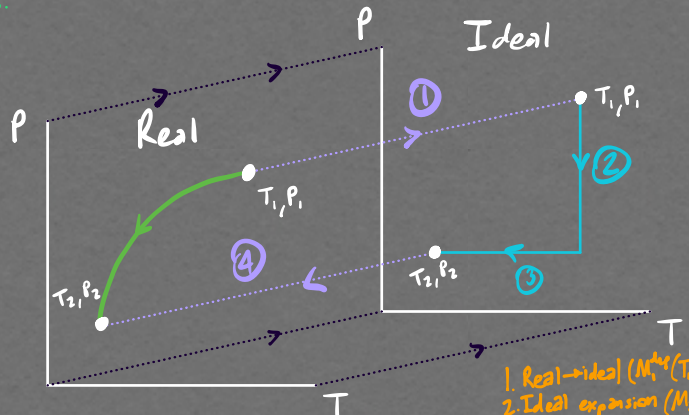
Lee-Kesler:  $Z = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r)$

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 acentric factor  $\omega$ , 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 points A to point B, the final value of  $\Delta M$  will be the same.

$\Delta M$  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 ( $M_1^{real}(T_1, P_1)$ )
2. Ideal expansion ( $M_2^{ideal}(T_1, P_1)$ )
3. Ideal cooling ( $M_3^{ideal}(T_2, P_1)$ )
4. Ideal → real ( $M_4^{real}(T_2, P_1)$ )

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

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

for molar entropy

$S^{dep}(T, P) = \int_0^P \left(\frac{R}{P} - \left(\frac{\partial v}{\partial T}\right)_P\right) dP$   
derived from your EOS of choice

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

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