Reminders

- HW 3B is be due on Monday, October 7

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Helpful sections of the book: Chapter 4 (Sections 4.6- 4.10)

Learning Objectives

- After the next two classes students should be able to:
  - Convert between the volumetric flowrate and mass flowrate for incompressible fluids
  - Look up physical properties in Table B.1
    - Specific gravity, molecular weight, critical T and P
  - Define an equation of state
  - State the assumptions of the ideal gas law
  - State when it is appropriate to apply the ideal gas law

Equations of state

- An **equation of state** is a function that relates the molar quantity and volume of a gas to temperature and pressure
  - What are n, P and V? →process variables!

- They are empirically derived!

René Magritte, 1928-29. Currently on display at Los Angeles County Museum of Art, USA

"The famous pipe. How people reproached me for it! And yet, could you stuff my pipe? No, it's just a representation, is it not? So if I had written on my picture 'This is a pipe', I'd have been lying!"

René Magritte

Christine Duval, 2024. Currently on display in AW Smith Building.

$$PV = nRT$$

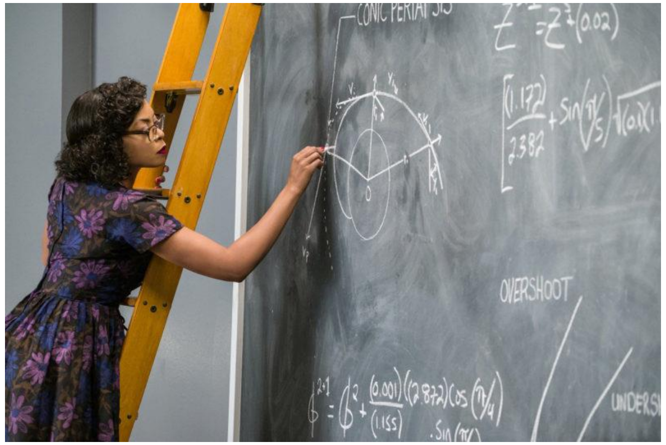
The gas is not ideal.

"Oh, ideal gas law. How often it is used in chemical engineering. And yet, is any gas truly ideal? No, the ideal gas law is how we choose to represent it. So if I tell the class, 'The gas is ideal', I'd have been lying!"

Christine Duval

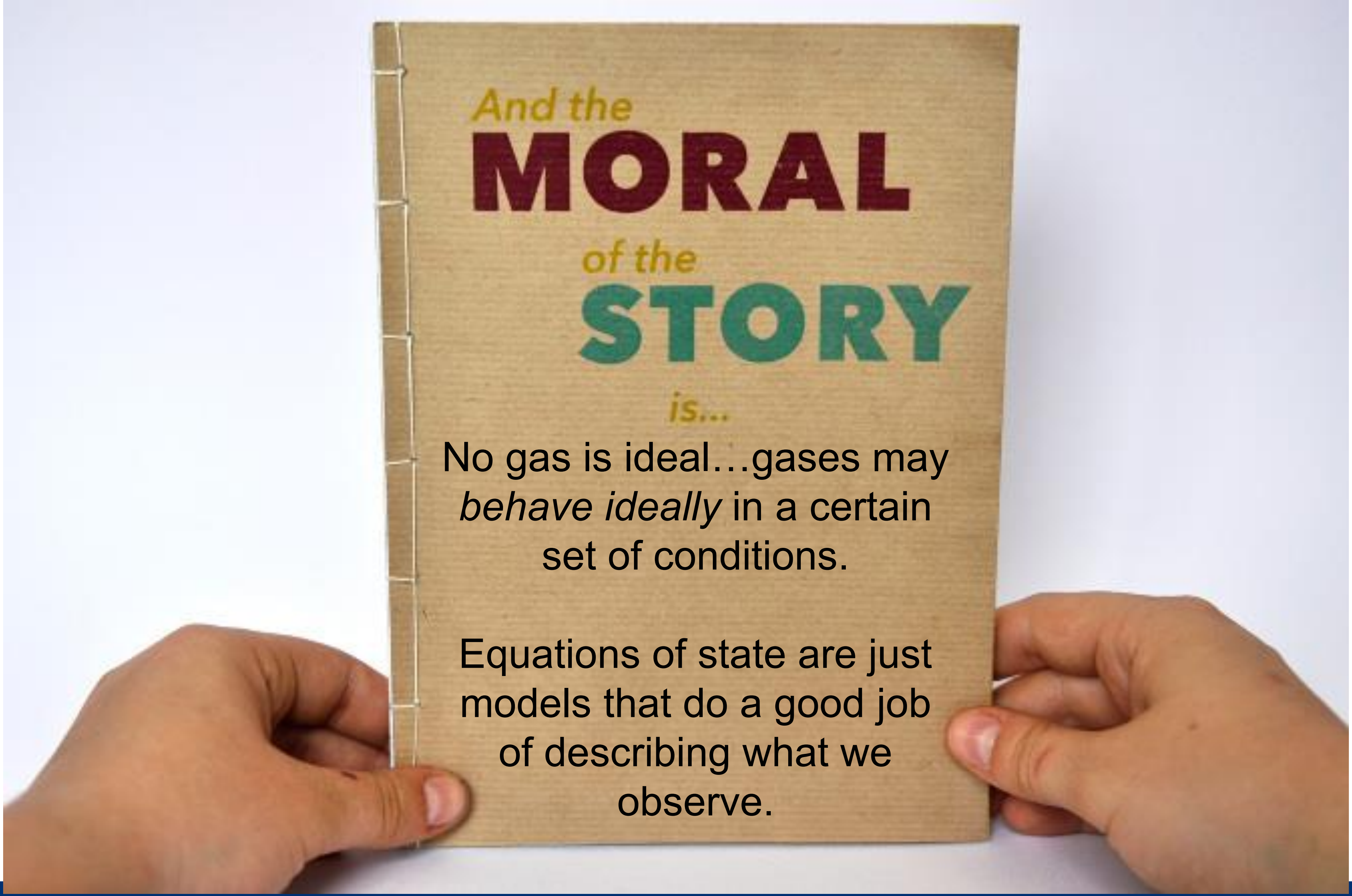
Thermodynamics: A play in 3 acts

Collect a lot of data on process variables (P, V, and T) in a specific range of conditions for many chemical species



Use known properties and math to create equations that fit all of the data – call them “equations of state”

Use the models and 2 of the process variables to predict the third process variable



No gas is ideal…gases may *behave ideally* in a certain set of conditions.

Equations of state are just models that do a good job of describing what we observe.

Ideal Gas Law

$$PV = nRT$$

- Assumptions
  - Large number of molecules in random motion
  - Volume of individual molecules << volume of gas
  - No intermolecular forces b/w molecules
  - Perfectly elastic collisions
  - Temperature of a gas depends kinetic energy of the molecules

- Conditions for which the ideal gas law applies:
  - "High" temperature (above 0 Celsius)
  - "Low" pressure (around 1 atm)

How do we know if a gas behaves ideally?

1. Calculate $\frac{RT}{P} = \hat{V}$

2. Assess. We can use the ideal gas law when…

$$\hat{V} = \frac{RT}{P} > 5\,\frac{L}{mol} \text{ for diatomic gases}$$

$$\hat{V} = \frac{RT}{P} > 20\,\frac{L}{mol} \text{ for other gases}$$

You may remember from chemistry class…

Table 5.2-1 Standard Conditions for Gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm	0.022415 m^3	1 mol
CGS	273 K	1 atm	22.415 L	1 mol
American Engineering	492°R	1 atm	359.05 ft^3	1 lb-mole

- This is only true at standard conditions for 1 mol of gas. The 22.415 L/mol is not a conversion factor
- We must use equations of state to relate V and moles for any other T and P

Equation of state

Equations of state are mathematical functions that relate molar volume, temperature, and pressure. ($\hat{V}$, T, P)

- If the ideal gas law does not apply…
  - **Virial EOS**
  - **Van der Waals EOS**
  - **Compressibility Factor EOS**
  - Soave-Redlich-Kwong (SRK) EOS
  - Many, many others

Van der Waals EOS

Accounts for V occupied by molecule

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

Accounts for intermolecular attraction

Useful when these assumptions <u>don't</u> apply:

- Volume of molecules << volume of gas
- No intermolecular forces between molecules

Van der Waals EOS

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

How do we find a and b?

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

Look it up!

Look it up!

Look it up!

Look it up!

Table B.1 in F&R

Compressibility Factor EOS

$$P\hat{V} = zRT$$

How do we find z?

z = f(Tr, Pr)

$$T_r = \frac{T}{\boxed{T_c}}$$ Look it up!

$$P_r = \frac{P}{\boxed{P_c}}$$ Look it up!

We can get more complicated…

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

Soave-Redlich-Kwong

Look it up!

Look it up!

$$a = 0.42747\frac{R^2 \boxed{T_c}^2}{\boxed{P_c}} \qquad b = 0.08664\frac{R\boxed{T_c}}{\boxed{P_c}}$$

Look it up!

Look it up!

$$\alpha = \left[1 + (0.48508 + 1.55171\boxed{\omega} - 0.1561\boxed{\omega^2})\left(1 - \sqrt{\frac{T}{\boxed{T_c}}}\right)\right]^2$$

Look it up!

Look it up!

Look it up!

Why do almost all EOS reference critical T and P?

- **Tc and Pc**: Highest temperature and corresponding pressure at which species can coexist in two phases (liquid and vapor)

- **Law of corresponding states**: Certain physical properties of a gas strongly depend on the proximity of the gas to its critical state

- What does the **Tr** and **Pr** tell us?

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

Law of corresponding states

- Certain physical properties of a gas strongly depend on the proximity of the gas to its critical state

The whole point

- We want to choose an EOS that works for our system
- What do we mean by "works"?
  - Allows us to predict properties (T,V,P, composition) <u>reliably</u>

This is not a pipe, but it's a great representation of one.

Equations of state are often *empirical* To determine the fitting parameters (a,b,z,etc…) we need to first **look up Pc and Tc**.

Table B.1 in F&R

Unit 4: Single phase systems and equations of state

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Compressibility Factor EOS

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$$P_r = \frac{P}{\boxed{P_c}}$$ Look it up!

Why do almost all EOS reference critical T and P?

- **Tc and Pc**: Highest temperature and corresponding pressure at which species can coexist in two phases (liquid and vapor)

- **Law of corresponding states**: Certain physical properties of a gas strongly depend on the proximity of the gas to its critical state

- Reduced temperature and pressure tell us how close we are to the critical state of the gas.

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

The whole point

- We want to choose an EOS that works for our system
- What do we mean by “works”?
  - Allows us to predict properties (T,V,P, composition) <u>reliably</u>

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