

# Ideal and Real Gases

## Learning Objectives

- Identify assumptions present in ideal gas model and assess how these break down for real gases
- Connect the equation of state for a real gas to conceptual and graphical models

## Ideal Gases

The equation of state for an ideal gas is given by:

$$PV = nRT$$

1. Using this equation, give the relationship between:

a. Temperature ( $T$ ) and Volume ( $V$ )

*As Temperature increases, Volume increases (directly proportional)*

b. Pressure ( $P$ ) and Temperature

*As Pressure increases, Temperature increases (directly proportional)*

c. Pressure and Volume

*As Pressure increases, Volume decreases (inversely proportional)*

2. In MATLAB, make a plot of Temperature vs. Volume. Use 1 mol of gas at 1 atm.

a. What happens to the volume as  $T \rightarrow 0$ ?

*The volume approaches 0.*

b. Will this be true for a real gas? Why or why not?

*No, real atoms have volume, and cannot be infinitely compressed.*

c. How does this behavior change as the pressure increases? Decreases?

*Qualitatively, as pressure increases, the slope of the line will increase, however it is still a linear relationship.*

## Real Gases

There are many equations of state that have been developed for real gases. One of the most common is the van der Waals equation of state shown below ( $a$  and  $b$  are always positive and constant dependent on the identity of the gas).

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

1. Looking at this equation, what happens when  $a$  and  $b$  are both equal to 0?

*If both  $a$  and  $b$  are 0, the ideal gas law is recovered.*

2. If  $a = 0$  and  $b > 0$ , how is the temperature affected relative to that of an ideal gas? Does this change if  $a > 0$  and  $b = 0$ ?

*Rearranging the equation given:  $T = \frac{1}{nR} \left( P + \frac{an^2}{V^2} \right) (V - nb)$*

*If  $a=0$  and  $b>0$ ,  $T = \frac{P(V-nb)}{nR}$ , and the effective volume is reduced and temperature decreases*

*If  $a>0$  and  $b=0$ ,  $T = \frac{PV}{nR} + \frac{an}{VR}$ , so the temperature will increase relative to an ideal gas*

3. In MATLAB, make a plot of Temperature vs. Volume. Use 1 mol of gas at 1 atm. Use  $a$  and  $b$  for  $N_2$ , given in the table below.

- a. What happens to the volume as  $T \rightarrow 0$ ?

*At 0 K, the equation is ill-defined, but the limit of  $V$  as  $T$  approaches 0 is  $\infty$*

- b. How does this compare with what must be true physically?

*Physically, the gas must have a fixed finite volume, but it also undergoes a phase transition which is not captured correctly by the van der Waals model*

4. The van der Waals constants for some real gases are included in the following table.

Gas	$a$	$b$
He	0.0341	0.0237
H <sub>2</sub>	0.2461	0.0267
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
CO <sub>2</sub>	3.59	0.0427
NH <sub>3</sub>	4.17	0.0371

- a. Which gas do you expect to behave the most like an ideal gas? Does this agree with your chemical intuition? Why or why not.

*Helium has the smallest value of  $a$  and  $b$  and should behave the most like an ideal gas. This is consistent with the fact that helium is small and has very weak interactions with other atoms.*

- b. Which gas do you expect to behave the least like an ideal gas? Why?

*NH<sub>3</sub> and CO<sub>2</sub> will behave the least like ideal gases. NH<sub>3</sub> should be less ideal since it has dipole-dipole interactions that are not present for CO<sub>2</sub>*

- c. Make a plot of Temperature vs. Volume for the gases in the table.

- d. Predict the values of  $a$  and  $b$  (roughly) for H<sub>2</sub>O? Justify your predictions.

*Water has stronger intermolecular interactions than any of the molecules in the table so should have  $a > 4.17$ . Predict around 5. The  $b$  constant roughly corresponds to the size and for water this should be .03-.04.*

5. State the two primary failings of the ideal gas law. Explain how  $a$  and  $b$  are used in the van der Waals equation of state to correct for each of these issues.

*1. the ideal gas law does not account for atomic/molecular size. The constant  $b$  affects the volume and accounts for the fact that real gases have size,*

*2. the ideal gas law does not account for intermolecular interactions. The constant  $a$  affects the pressure and accounts for intermolecular interactions in real gases.*