

1. Two identical containers, one red and one yellow, are inflated with different gases at the same volume and pressure. Both containers have an identically sized hole that allows the gas to leak out. It takes four times as long for the yellow container to leak out compared to the red container. If the red container is twice as hot as the yellow container, what is the ratio of the molar masses of the gases ( $M_{\text{yellow}} / M_{\text{red}}$ ).

$$\frac{\text{rate1}}{\text{rate2}} = \frac{\bar{u}_1}{\bar{u}_2} = \frac{t_2}{t_1}; \quad \bar{u}^2 = \frac{3RT}{M}; \quad u = \sqrt{\frac{3RT}{M}} \quad \text{and} \quad \underline{\mathbf{T(\text{red})=2*T(\text{yellow}) ; t(\text{yellow})=4*t(\text{red}) \text{ or}}}$$

$$\underline{\mathbf{Rate(R)=4Rate(Y)}}$$

$$\frac{\text{Rate(R)}}{\text{Rate(Y)}} = \frac{t_Y}{t_R} = \frac{4}{1} = \sqrt{\frac{\frac{M(Y)}{T(Y)}}{\frac{M(R)}{T(R)}}} = \sqrt{\frac{M(Y) * T(R)}{M(R) * T(Y)}} = \sqrt{\frac{M(Y) * 2 * T(Y)}{M(R) * T(Y)}} = \sqrt{\frac{2M(Y)}{M(R)}} = \frac{2M(Y)}{M(R)} = 16$$

$$\frac{M(Y)}{M(R)} = 8$$

2. A container is filled with He at 18 °C and 7.92 bar. It is found that the pressure of the container drops by 50% in 35 minutes, due to a small hole. If the container had instead been filled with Ne at 18 °C and 7.92 bar, what would be the pressure of the Ne after 35 minutes? Express your answer in bar.

a.  $|\Delta P_{\text{He}}| = 0.50 * 7.92 \text{ bar} = 3.96$  drops by 50%  $\Delta P = P_f - P_{in} = 3.96 - 7.92 = -3.96$  ;

b.  $\frac{\text{rate1}}{\text{rate2}} = \frac{\bar{u}_1}{\bar{u}_2}$ ;  $\text{Rate} = \Delta \frac{[\text{amount}]}{\text{time}}$

c.  $\frac{\text{rateHe}}{\text{rateNe}} = \frac{\frac{\Delta P_{\text{He}}}{t}}{\frac{\Delta P_{\text{Ne}}}{t}} = \frac{\Delta P_{\text{He}}}{\Delta P_{\text{Ne}}} = \sqrt{\frac{M_{\text{Ne}}}{M_{\text{He}}}} = 2.246$

d.  $|\Delta P_{\text{Ne}}| = |\Delta P_{\text{He}}| \sqrt{\frac{M_{\text{He}}}{M_{\text{Ne}}}} = 1.76$  or 22.26% ;  $\Delta P_{\text{Ne}} = -1.76$  because pressure of the container drops

e.  $P_{\text{Ne}} = P_{in} + \Delta P = (7.92 + (-1.76)) \text{ bar} = 6.16 \text{ bar}$

3. Solve the van der Waals real gas equation  $\left( P_{\text{observed}} + a \left[ \frac{n}{V} \right]^2 \right) (V_{\text{container}} - bn) = nRT$ , for the pressure.

$$P_{\text{observed}} = \frac{nRT}{(V_{\text{container}} - bn)} - a \left[ \frac{n}{V} \right]^2$$

- a. To investigate how the **a** coefficient affects the pressure, set the **b** coefficient to zero. Does **a** increase or decrease the pressure compared to what you would expect for an ideal gas?

$$P_{\text{observed}} = \frac{nRT}{V_{\text{container}}} - a \left[ \frac{n}{V} \right]^2 \quad \mathbf{a} \uparrow \quad \mathbf{P} \downarrow \quad P_{\text{observed}} < P_{\text{ideal}} \quad \mathbf{a} \text{ is responsible for lowering the pressure}$$

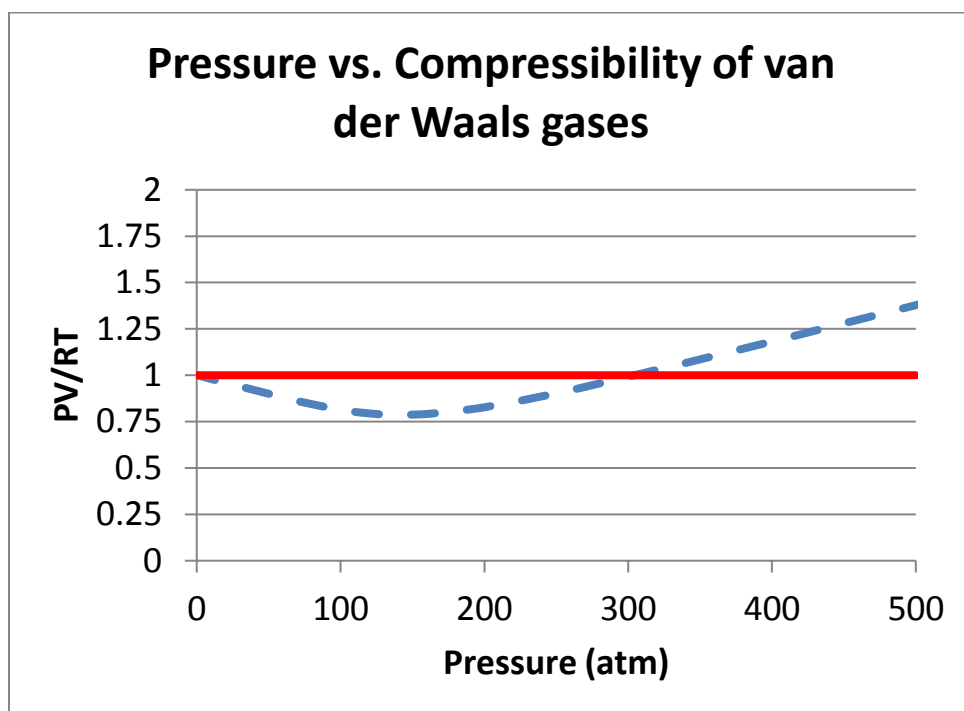
Stronger the intermolecular forces greater the value of **a**.

- b. To investigate how the **b** coefficient affects the pressure, set the **a** coefficient to zero. Does **b** increase or decrease the pressure compared to what you would expect for an ideal gas?

$$P_{\text{observed}} = \frac{nRT}{V_{\text{container}} - bn} \quad b \uparrow \quad P \uparrow \quad P_{\text{observed}} > P_{\text{ideal}} \quad a \text{ is responsible for increasing the pressure}$$

Bigger the volume of the molecules the greater the value of **b**

- c. Below is a plot of the compressibility ( $PV/RT$ ) as a function of changing pressure for 1 mole of a real gas (dashed line) and an ideal gas (solid line). Using what you learned in parts (a) and (b), at what pressures is the **a** coefficient dominant and at what pressures is the **b** coefficient dominant. (y axis is  $(PV/RT)_{\text{real}} / (PV/RT)_{\text{ideal}}$ )



**a** dominates at low pressures and **b** dominates at high pressures

4. Put the following molecules in increasing order of van der Waals constant, **b**?  $\text{Cl}_2$ ,  $\text{N}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ .

$\text{N}_2 < \text{Cl}_2 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8$ , Bigger the volume of the molecules the greater the value of **b**

5. For each of the pair of molecules below, which has the highest value of van der Waals constant, **a**? Identify the dominant intermolecular forces.

**H<sub>2</sub>O** vs  $\text{CO}_2$

Ne vs **F<sub>2</sub>**,

C<sub>6</sub>H<sub>6</sub> vs CH<sub>3</sub>OH

6. Which of the following gases will behave least ideally under the same conditions? Explain your choice using the **a** and **b** van der Waals coefficients. ( the molecules with greatest volume and stronger Intermolecular forces)

CH<sub>4</sub> or SO<sub>2</sub>

Cl<sub>2</sub> or N<sub>2</sub>

7. Match the molecules below with their **a** and **b** van der Waals coefficients.

(Hint: Look at the value of **b** first and decide based on the size of the molecules and then think about Intermolecular forces )

<u>Gas</u>	<u>a (L<sup>2</sup> atm mol<sup>-2</sup>) / b (L mol<sup>-2</sup>)</u>
Water (H <sub>2</sub> O)	→ 0.2476 / 0.02661
Argon (Ar)	→ 5.536 / 0.03029
Hydrogen (H <sub>2</sub> )	→ 1.363 / 0.03219
Benzene (C <sub>6</sub> H <sub>6</sub> )	→ 18.24 / 0.1154

8. O<sub>2</sub> and H<sub>2</sub>O have similar values of van der Waals constant, **b**, but different van der Waals constant, **a** which one will have higher pressure at the same temperature and volume.

P(H<sub>2</sub>O) < P(O<sub>2</sub>)    **a** ↑    P ↓    P<sub>observed</sub> < P<sub>ideal</sub>    **a** is responsible for lowering the pressure  
Stronger the intermolecular forces greater the value of **a**.

9. NO<sub>2</sub> and Trifluoromethane (CF<sub>3</sub>H) have similar values of Van der Waals constant, **a**, but different van der Waals constant, **b** which one will have higher pressure at the same temperature and volume.

P(NO<sub>2</sub>) < P(CF<sub>3</sub>H)    **b** ↑    P ↑    P<sub>observed</sub> > P<sub>ideal</sub>    **a** is responsible for increasing the pressure  
Bigger the volume of the molecules the greater the value of **b**

10. ( At home ) A 5.0mol sample of NH<sub>3</sub> gas is kept at 2.0 L container and 27°C , Calculate the pressure in bars of the gas assuming it does not behave ideally. ( $a=4.0 \text{ bar}\cdot\text{L}^2/\text{mol}^2$  and  $b= 0.040\text{L/mol}$ )

$$P_{observed} = \frac{nRT}{(V_{container} - bn)} - a \left[ \frac{n}{V} \right]^2$$

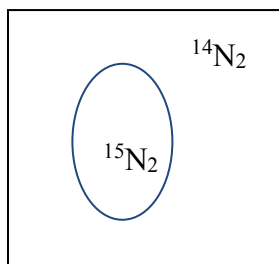
$$P_{observed} = \frac{5.0mol \cdot 0.08314 \text{ (L}\cdot\text{bar)} / (\text{mol}\cdot\text{K}) \cdot 300.15\text{K}}{(2.0\text{L} - 0.040(\text{L/mol}) \cdot 5.0mol)} - 4.0 (\text{bar}\cdot\text{L}^2/\text{mol}^2) \cdot \left[ \frac{5.0mol}{2.0\text{L}} \right]^2 = 44.3179\text{bar}$$

$$P_{ideal} = \frac{nRT}{V_{container}} = 62.386$$

What is the percent error compared to an ideal gas? % error = 100% \* |(P<sub>observed</sub> - P<sub>ideal</sub>)|/P<sub>ideal</sub>

11. Consider a balloon filled with  $^{15}\text{N}_2$  gas and placed in larger container filled only with  $^{14}\text{N}_2$ . If a small hole is made in the balloon, initially as the gases effuse, will the balloon expand, contract or stay the same volume? **Assume the pressures inside the balloon and in the container are the same.** Explain your answer. It may help to draw a picture.

**Increase**



12. Two identical containers, one red and one yellow, are filled with different noble gases at the same temperature and pressure. Both containers have an identically sized hole in them allowing the gases to leak out. If it takes the red container 10.0 seconds to empty and the yellow container 57.3 seconds to empty, what are the noble gases contained in each container? (Remember: rate is proportional to  $1/\text{time}$ )

$$\frac{\text{rate1}}{\text{rate2}} = \frac{\bar{u}_1}{\bar{u}_2}; \quad \bar{u}^2 = \frac{3RT}{M}; \quad \mathbf{T(\text{red})=T(\text{yellow})}$$

$$\text{Rate(Red)} = \frac{1}{\text{time}(\text{red})} = \frac{1}{10}; \quad \mathbf{u_{\text{red}} = \sqrt{\frac{3RT}{M(\text{red})}}}$$

$$\text{Rate(yellow)} = \frac{1}{\text{time}(\text{yellow})} = \frac{1}{57.3}; \quad \mathbf{u_{\text{yellow}} = \sqrt{\frac{3RT}{M(\text{yellow})}}}$$

$$\frac{\text{RateR}}{\text{RateY}} = \frac{\left(\frac{1}{10}\right)}{\left(\frac{1}{57.3}\right)} = \frac{57.3}{10} = \frac{u(\text{red})}{u(\text{yellow})} = \sqrt{\frac{M_Y}{M_R}}$$

$$\frac{M_Y(\text{Xe})}{M_R(\text{He})} = (5.73)^2 = 32.8 \text{ (exact)} \sim 25 - 36 \text{ (depends on rounding)}$$

$$\mathbf{\text{He: } 4 * 30 = 120 \text{ (Xe)}}$$

13. In 2.00 min, 29.7mL of helium effuses through a small hole. Under the same conditions (temperature and pressure), a 10.00 mL of a mixture of CO and CO<sub>2</sub> effuse through the same hole in the same amount of time. Calculate the percent composition by volume of the mixture.

$$\mathbf{PV=nRT}; \quad \mathbf{V = \frac{nRT}{P}}; \quad \mathbf{\text{rate} \sim \frac{V}{\text{time}}}$$

$$\sqrt{\frac{M_{\text{mix}}}{M_{\text{He}}}} = \frac{\text{rate}(\text{He})}{\text{rate}(\text{mix})} = \frac{\frac{29.7\text{mL}}{2.00\text{min}}}{\frac{10.00\text{mL}}{2.00\text{min}}} = 2.9$$

$$\mathbf{M(\text{mix}) = (2.97)^2 * 4 \frac{\text{g}}{\text{mol}} = 35.3 \text{ g/mol}}$$

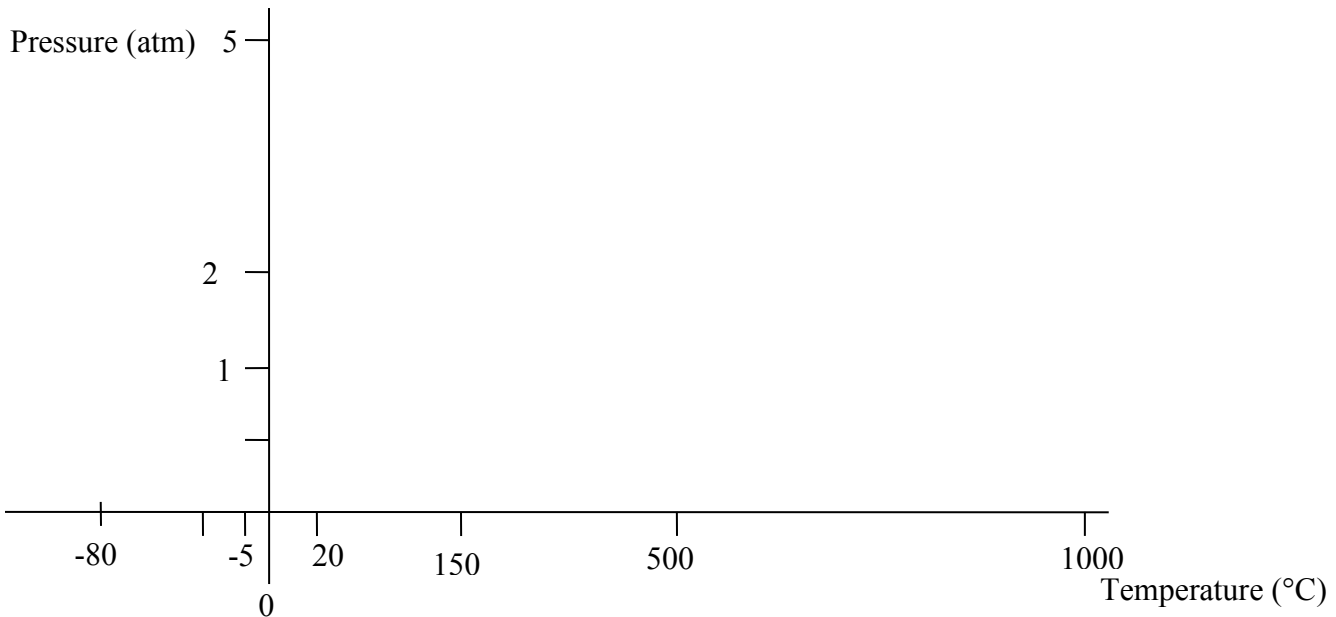
$$\mathbf{\chi_{\text{CO}} + \chi_{\text{CO}_2} = 1} \quad \mathbf{\chi_{\text{CO}} * (28\text{g/mol}) + \chi_{\text{CO}_2} * (44 \text{ g/mol}) = 35.3 \text{ g/mol}}$$

$$\mathbf{\chi_{\text{CO}} = 45.5\%} \quad \mathbf{\chi_{\text{CO}_2} = 54.5\%}$$

14. Two identical containers are filled with the same number of moles of gas at the same temperature. Container A contains a gas with a molar mass of 40. g/mol, and container B contains a gas with a molar mass of 160. g/mol. A hole of identical size is then made in each container. What is the ratio  $t_{A}/t_{B}$  of the times necessary for the number of moles of gas to drop to half in each container?

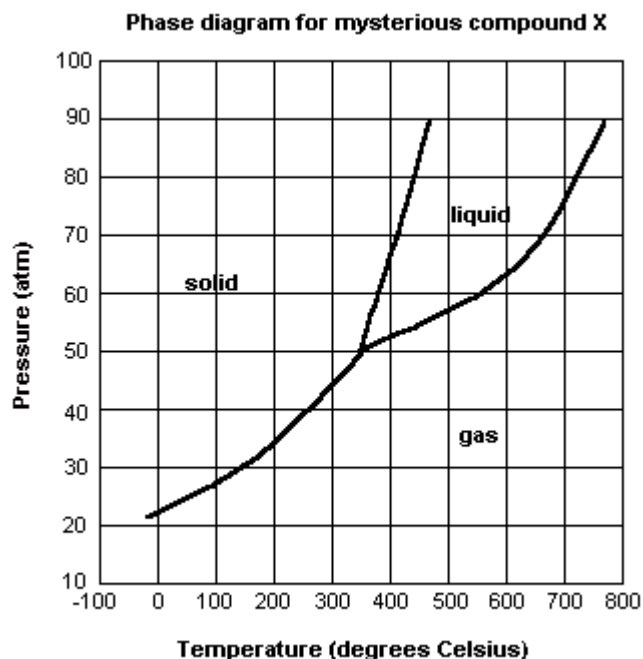
$$\frac{\text{Rate B}}{\text{Rate A}} = \frac{t_a}{t_b} = \sqrt{\frac{M_a}{M_b}} = 0.5$$

15. Imagine a substance with the following points on the phase diagram: a triple point at .5 atm and  $-5^{\circ}\text{C}$ ; a normal melting point at  $20^{\circ}\text{C}$ ; a normal boiling point at  $150^{\circ}\text{C}$ ; and a critical point at 5 atm and  $1000^{\circ}\text{C}$ . For this, complete the following:
- What does it mean to have a normal solid-liquid line?
  - Roughly sketch the phase diagram, using units of atmosphere and  $T^{\circ}\text{C}$ .



- Rank the states with respect to increasing density: **s > l > g**
- Describe what one would see at pressures and temperatures above 5 atm and  $1000^{\circ}\text{C}$ . **supercritical fluid separation between liquid and gas disappears.**
- Describe what will happen to the substance when it begins in a vacuum at  $-15^{\circ}\text{C}$  and is slowly pressurized. **g  $\rightarrow$  s**
- Describe the phase changes from  $-80^{\circ}\text{C}$  to  $500^{\circ}\text{C}$  at 2 atm. **S  $\rightarrow$  L  $\rightarrow$  g**

16. For each of the following questions refer to the phase diagram for mysterious compound X.



If you were to have a bottle containing compound X in your closet, what phase would it most likely be in? **above 750°C**

- 3) At what temperature and pressure will all three phases coexist? **50 atm; 350 °C**
- 4) If I have a bottle of compound X at a pressure of 45 atm and temperature of 100°C, what will happen if I raise the temperature to 400°C? **s → g sublimation**
- 5) Why can't compound X be boiled at a temperature of 200°C? **No, because liquid phase is at 200°C**
- 6) If I wanted to, could I drink compound X? **NO**