

## Oxidation Reduction Reactions

Conclusion of ch 4

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## Hanson Activity 4-4

- Discuss Key Questions 1-4 of Activity 4-4, page 68, with your partner for five minutes.
- The clicker quiz will commence at 8:50 AM sharp

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What is the oxidation number the pure element  $S_8$ ?

1. -2
2. -1
3. 0
4. +1
5. +2
6. +8

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For the ion  $\text{SO}_4^{2-}$ , what is the sum of the oxidation numbers of S and the four O atoms?

1. +2
2. +1
3. 0
4. -1
5. -2
6. None of the above

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Why does Cl have a negative oxidation number in  $\text{CCl}_4$ , but a positive oxidation number in  $\text{HClO}$ ?

- |  |    |
|--|----|
| 1. Cl is <u>more</u> electronegative than C, but <u>less</u> electronegative than O. | 0% |
| 2. Cl is <u>less</u> electronegative than C, but <u>more</u> electronegative than O. | 0% |
| 3. There are more Cl atoms in $\text{CCl}_4$   | 0% |
| 4. $\text{HClO}$ is an acid  | 0% |
| 5. It just one of the "mysteries" of chemistry.                                      | 0% |

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Table 4.3

Rules for Assigning Oxidation States

1. The oxidation state of an atom in an element is 0. For example, the oxidation state of each atom in the substances  $\text{Na}(s)$ ,  $\text{O}_2(g)$ ,  $\text{O}_3(g)$ , and  $\text{Hg}(l)$  is 0.
2. The oxidation state of a monatomic ion is the same as its charge. For example, the oxidation state of the  $\text{Na}^+$  ion is +1.
3. In its covalent compounds with nonmetals, hydrogen is assigned an oxidation state of +1. For example, in the compounds  $\text{HCl}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$ , hydrogen is assigned an oxidation state of +1.
4. Oxygen is assigned an oxidation state of -2 in its covalent compounds, such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{SO}_3$ . The exception to this rule occurs in peroxides (compounds containing the  $\text{O}_2^{2-}$  group), where each oxygen is assigned an oxidation state of -1. The best-known example of a peroxide is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).
5. In binary compounds, the element with the greater attraction for the electrons

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state of  $-1$ . The best-known example of a peroxide is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

- In binary compounds, the element with the greater attraction for the electrons in the bond is assigned a negative oxidation state equal to its charge in its ionic compounds. For example, fluorine is always assigned an oxidation state of  $-1$ . That is, for purposes of counting electrons, fluorine is assumed to be  $\text{F}^-$ . Nitrogen is usually assigned  $-3$ . For example, in  $\text{NH}_3$ , nitrogen is assigned an oxidation state of  $-3$ ; in  $\text{H}_2\text{S}$ , sulfur is assigned an oxidation state of  $-2$ ; in  $\text{HI}$ , iodine is assigned an oxidation state of  $-1$ ; and so on.
- The sum of the oxidation states must be zero for an electrically neutral compound and must be equal to the overall charge for an ionic species. For example, the sum of the oxidation states for the hydrogen and oxygen atoms in water is 0; the sum of the oxidation states for the carbon and oxygen atoms in  $\text{CO}_3^{2-}$  is  $-2$ ; and the sum of oxidation states for the nitrogen and hydrogen atoms in  $\text{NH}_4^+$  is  $+1$ .

Chemical Species	Oxidation Number	Rationale
$\text{O}_2$	0	The oxidation number of an atom of a pure element is always 0 because there is no electronegativity difference when all the atoms are the same.
Element	0	
He	0	
$\text{Mg}^{2+}$	+2	The oxidation number of an atom or a monatomic ion is its charge.
$\text{Cl}^-$	-1	
$\text{H}_2\text{O}$	H = +1	
$\text{CH}_4$		Hydrogen in a compound has an oxidation number of +1 unless it is combined with a metal having a smaller electronegativity, in which case it is $-1$ .
LH	H = +1	
NaH	H = -1	
HF	F = -1	Fluorine in a compound always has an oxidation number of $-1$ because it is the most electronegative element.
$\text{CF}_4$	F = -1	
$\text{H}_2\text{O}$	O = -2	
$\text{H}_2\text{O}_2$	O = -1	Oxygen in a compound has an oxidation number of $-2$ unless it is a peroxide, in which case it is $-1$ , or is combined with fluorine.
$\text{Na}_2\text{O}_2$		
$\text{Cl}_2$	$+2(\text{O}) - 1(\text{F}) + 2 = 0$	In a polyatomic molecule or ion, the sum of all the oxidation numbers of the atoms is equal to the charge on the molecule or ion.
$\text{BrCl}$	Cl = -1 Br = +1	If the above rules do not determine all the oxidation numbers, the most electronegative atom is assigned an oxidation number equal to the charge it would have if it had 0 valence electrons.

Table 16.4 Oxidation States

## Exercise 1, page 69, using Model 1

- At the projector:  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{SF}_6$
- With your partner complete Ex 1

In  $\text{SO}_4^{2-}$ , the oxidation number of S is:

1. +2
2. +4
3. +6
4. -2
5. -4

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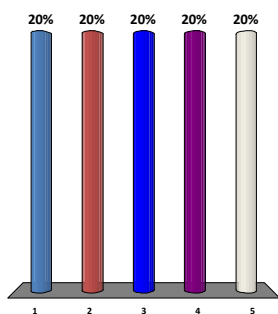
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In  $\text{H}_2\text{S}$ , the oxidation number of S is:

1. +2
2. +4
3. +6
4. -2
5. -4



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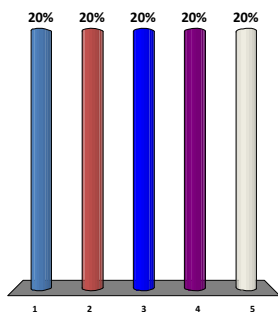
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In  $\text{Na}_2\text{SO}_3$ , the oxidation number of S is:

1. +2
2. +4
3. +6
4. -2
5. -4



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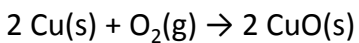
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### Model 2, p. 70 Key Questions



- How many electrons are transferred from one copper atom to one oxygen atom?
- What are the oxidation numbers in all three species?

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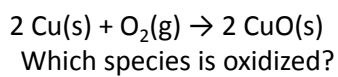
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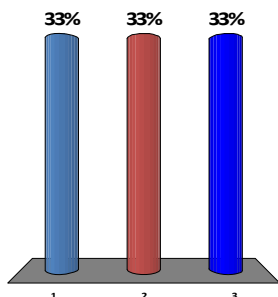
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- CuO(s)
- Cu(s)
- O<sub>2</sub>(g)




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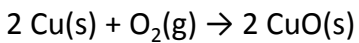
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### Model 2, p. 70 Key Questions



- Which species is reduced?
- What is the oxidizing agent? The reducing agent?

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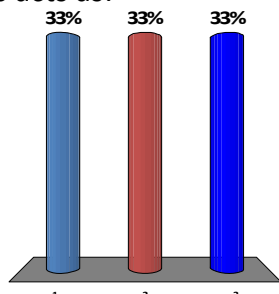
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If the oxidation number of a species increases during a reaction, that species acts as:

1. A reducing agent
2. An oxidizing agent
3. Either one, depending on the other species




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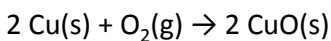
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### Model 2, p. 70 Key Questions



7. Which species is reduced?
8. What is the oxidizing agent? The reducing agent?
9. If a species has an increase in oxidation number, is it an oxidizing agent or reducing agent?
10. How can we distinguish redox reactions from the other types.

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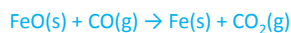
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### Exercise 2, page 70, at projector



- Assign ox numbers
- Identify species oxidized/reduced
- Identify oxidation/reduction agents
- Is it balanced?
- Can you tell from the number of electrons transferred?
- Do Exercises 2b-2f with partner. (2f is unbalanced)

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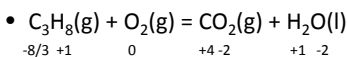
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### Problem 4-69c to balance:



-8/3 +1      0      +4 -2      +1 -2  
 What is oxidized? How many electrons are lost per atom?

4 - (-8/3) or (20/3) per C atom

What is reduced? How many electrons are gained/atom?

2 per O atom

What is the ratio of O atoms/Catom?

# electrons lost = # electrons gained

#C atoms x (20/3) = #O atoms x (2)

#O atoms = (#C atoms) (20/3)(1/2) = (10/3)(#C atoms)

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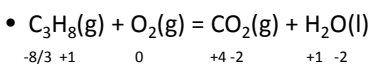
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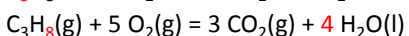
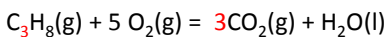
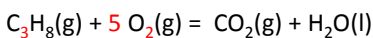
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### Problem 4-69c to balance:



-8/3 +1      0      +4 -2      +1 -2  
 #O atoms = (10/3)(#C atoms)




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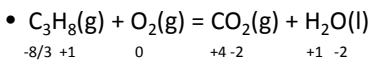
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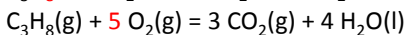
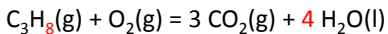
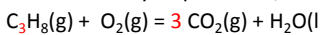
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### Problem 4-69c to balance:



-8/3 +1      0      +4 -2      +1 -2  
 Can be done by inspection w/o oxidation numbers



Do the electrons exchanged balance?

C: 3 atoms from -8/3 to +4 = 3 x (20/3) = 20

O: 10 atoms from 0 to -2 = 10 x (2) = 20

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### Problem 71-a in acid soln

- $\text{Cu(s)} + \text{NO}_3^-(\text{aq}) = \text{Cu}^{2+}(\text{aq}) + \text{NO(g)}$
- 0      +5 -2                      +2                      +2 -2
- Each copper atom loses 2 electrons (0  $\rightarrow$  +2)
- Each nitrogen atom gains 3 electrons (+5  $\rightarrow$  +2)
- What must be the ration of N to Cu atoms?
- **3 Cu: 2 N**
- $3 \text{Cu(s)} + 2 \text{NO}_3^-(\text{aq}) = 3\text{Cu}^{2+}(\text{aq}) + 2 \text{NO(g)}$
- Is charge balanced? Are oxygen atoms balanced?

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### Problem 71-a in acid soln

- $3 \text{Cu(s)} + 2 \text{NO}_3^-(\text{aq}) = 3\text{Cu}^{2+}(\text{aq}) + 2 \text{NO(g)}$
- In acid solution: Hydrogen ions are available to balance charge, yielding water as needed.
- $3 \text{Cu(s)} + 2 \text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) = 3\text{Cu}^{2+}(\text{aq}) + 2 \text{NO(g)}$
- $3 \text{Cu(s)} + 2 \text{NO}_3^-(\text{aq}) + 8\text{H}^+(\text{aq}) = 3\text{Cu}^{2+}(\text{aq}) + 2 \text{NO(g)} + 4\text{H}_2\text{O(l)}$
- In base solution,  $\text{OH}^-(\text{aq})$  would be available.

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### Hanson Activity 11-1

- Discuss Key Questions 1-7 of Activity 11-1, page 209, with your partner for five minutes.
- The clicker quiz will commence in 5 minutes

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### Clicker quiz

- You may refer to your Hanson workbook
- Answer the questions **individually**
- In each case indicate the **best** answer
- **No** paper responses will be accepted

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According to the ideal gas law, if the temperature increases while  $n$  and  $V$  remain unchanged, what happens to pressure?

- 33% 1. Decreases
- 33% 2. Remains unchanged
- 33% 3. Increases

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According to the ideal gas law, if the volume increases while  $n$  and  $T$  remain unchanged, what happens to pressure?

- % 1. Decreases
- % 2. Remains unchanged
- % 3. Increases

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According to the ideal gas law, if the number of molecules in the container increases while  $P$  and  $T$  remain unchanged, what happens to volume?

33% 1. Decreases

33% 2. Remains unchanged

33% 3. Increases

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According to the ideal gas law, if the number of molecules in the container increases while  $V$  and  $T$  remain unchanged, what happens to pressure?

33% 1. Decreases

33% 2. Remains unchanged

33% 3. Increases

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At what temperature does an ideal gas exert no pressure?

33% 1. 273.15 K

33% 2. Zero Kelvin

33% 3. Zero Celsius

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Exercise 1, page 209 at Projector

Calculate a value for R and determine its units using the following data:

n = 1.000 mole

P = 0.1300 atm

V = 172.42 L

T = 273.15 K

Answer:  $R = 0.08206 \text{ L-atm/mol-K}$

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Do Ex 2, p210, with partner

- What is the volume?
- 22.4 L for 1 mole at STP

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Do  
Got it #1, p210, with partner

- What are the answers?

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Do

Got it #2, p210, with partner

- What are the answers?

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Problem #2, p. 211 with partner

- Draw the experimental setup first!
- Strategy: treat each gas separately.
- $P_T = P_1 + P_2 = 2.8 \text{ atm} + 6.0 \text{ atm} = 8.8 \text{ atm}$

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Problem #3, p. 212 with partner

- What is the relationship between moles of a gas (n), its mass (m), and molar mass (M)?
- What is the relationship between moles of a gas(n), its pressure , volume, and temperature?

$$n = \frac{m}{M} \quad n = \frac{PV}{RT} \quad \frac{m}{V} = \frac{PM}{RT}$$

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**Problem #4, p. 212 with partner**

- First obtain the molar mass  $M$  of this compound, using the relationship from Problem 3

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**Problem #4, p. 212 with partner**

- If  $M = 32.0$  g/mol
- The compound contains only N and H
- The compound is 87.4% N by mass
- **What is the molecular formula?**

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$$PV = nRT$$

- The only gas law to be memorized
- If  $n$  and  $T$  are constant:  $PV = k$  (Boyle)
- If  $P$  and  $n$  are constant:  $V = (nR/P)T = bT$  (Charles)
- If  $T$  and  $P$  are constant:  $V = n(RT/P) = an$  (Avogadro)

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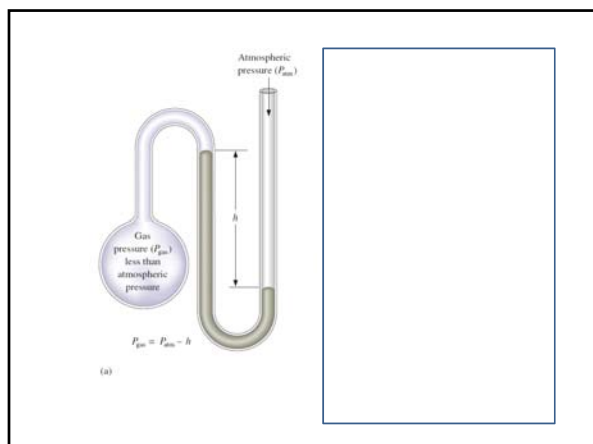
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$V = 22.41$  L for ideal gas

**TABLE 5.2**

Molar Volumes for Various Gases at 0°C and 1 atm

Gas	Molar Volume (L)
Oxygen ( $\text{O}_2$ )	22.397
Nitrogen ( $\text{N}_2$ )	22.402
Hydrogen ( $\text{H}_2$ )	22.433
Helium (He)	22.434
Argon (Ar)	22.397
Carbon dioxide ( $\text{CO}_2$ )	22.260
Ammonia ( $\text{NH}_3$ )	22.079

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### Hanson Activity 11-3

- Discuss Key Questions 1-6 of Activity 11-3, page 220, with your partner for five minutes.
- The clicker quiz will commence in 5 minutes

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### Clicker quiz

- You may refer to your Hanson workbook
- Answer the questions **individually**
- In each case indicate the **best** answer
- **No** paper responses will be accepted

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### Partial Pressures (Dalton)

- Consider a container with two ideal gases.
- The pressures are independent of each other:
- $P_T = P_1 + P_2$
- Treat each pressure by ideal gas law:
- $P_T = n_1(RT/V) + n_2(RT/V) =$   
 $(n_1 + n_2)(RT/V) = n_T(RT/V)$

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### Partial Pressures (Dalton)

- $P_T = n_1(RT/V) + n_2(RT/V) = P_1 + P_2 =$   
 $(n_1 + n_2)(RT/V) = n_T(RT/V)$
- The *mole fraction* of a gas is the ratio of number of moles of that gas to the total number of moles.
- $\chi_1 = n_1/n_T$ , and  $\chi_2 = n_2/n_T$ ,
- $P_1 = \chi_1 P_T$  and  $P_2 = \chi_2 P_T$

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### Exercise 1 at projector

- $\chi(\text{O}_2) = 0.209$  in air
- What are partial pressures of oxygen and nitrogen when  $P=755$  torr?
- 158 and 597 torr

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### Do Exercise #2 with partner

- Remember: nitrogen and oxygen are independent in this model.

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### Problem #1, p. 221

- 1<sup>st</sup> – calculate the total pressure in the cylinder
- 2<sup>nd</sup> – calculate the mole fractions of each gas
- 3<sup>rd</sup> – calculate the partial pressure of each gas

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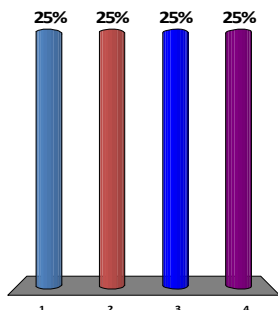
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What is the total pressure?

1. 2.33 atm
2. 4.66 atm
3. 7.00 atm
4. 9.33 atm




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- Finish problem #1

$$\chi_i = n_i/n_{\text{total}} = P_i/P_{\text{total}}$$

$$P(\text{CO}_2) = 2.33 \text{ atm}$$

$$P(\text{N}_2) = 4.67 \text{ atm}$$

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- Problem #2: start by calculating the partial pressure of oxygen in the tank

– How many moles of oxygen?

– What is its partial pressure?

– Repeat for nitrogen and add partial pressures to get total pressure

$$P_T = 16 \text{ atm.}$$

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**Problem #3, page 222**  
 $2 \text{KClO}_3(s) = 2 \text{KCl}(s) + 3 \text{O}_2(g)$

- Oxygen is collected over water.
- Gas contains the oxygen generated plus the equilibrium vapor pressure of water at this temp.

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**Problem #3, page 222**

- Oxygen is collected over water.
- Gas contains the oxygen generated plus the equilibrium vapor pressure of water at this temp.
- 1<sup>st</sup>: what is the partial pressure of oxygen?
- 2<sup>nd</sup>: How many moles of oxygen
- 3<sup>rd</sup>: How many moles of potassium chlorate?

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**What is the partial pressure of oxygen?**

1. 755.3 torr
2. 23.8 torr
3. 779.1 torr
4. 731.5 torr
5. 760 .0 torr

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### Problem #3, page 222

- 1<sup>st</sup>: what is the partial pressure of oxygen?
- 2<sup>nd</sup>: How many moles of oxygen?
- 0.0394 mol O<sub>2</sub>
- 3<sup>rd</sup>: How many moles of potassium chlorate?
- 0.0262 mol KClO<sub>3</sub>

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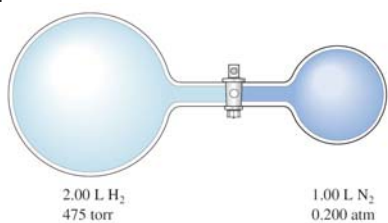
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### Problem 5-29

317 torr H<sub>2</sub>; 50.7  
torr N<sub>2</sub>

- What are final partial pressures of H<sub>2</sub> and N<sub>2</sub>.
- V<sub>f</sub> = 3.00 L.




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### Problem 5-37

970 K

- Bursts at 2500 torr
- T = 21.0 °C
- P = 758 torr
- Then heated
- At what Temp will it burst?

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## Problem 5-57

- Sample of CH<sub>4</sub> contains small amount of He
- Density = 0.70902 g/L at 0.0°C and 1.000 atm
- What is the volume % of He?
- 98.84% methane

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## Problem 4-59

- Fe(s) + H<sub>2</sub>SO<sub>4</sub>(aq) = FeSO<sub>4</sub>(aq) + H<sub>2</sub>(g)
- Volume of hydrogen = 4800 m<sup>3</sup> x 1.20 =?
- T=0°C, and P = 1.0 atm: moles of H<sub>2</sub>?
- What mass of iron was needed?
- 1.5 x 10<sup>7</sup> g Fe

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## Real Gases vs Ideal Gases

- For an ideal gas:

$$PV = nRT$$

$$\frac{PV}{nRT} = 1$$

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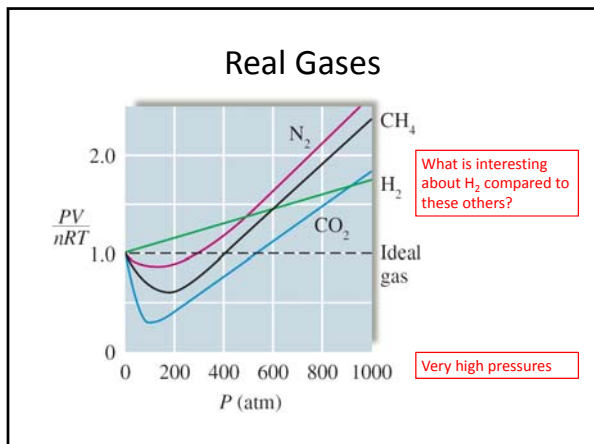
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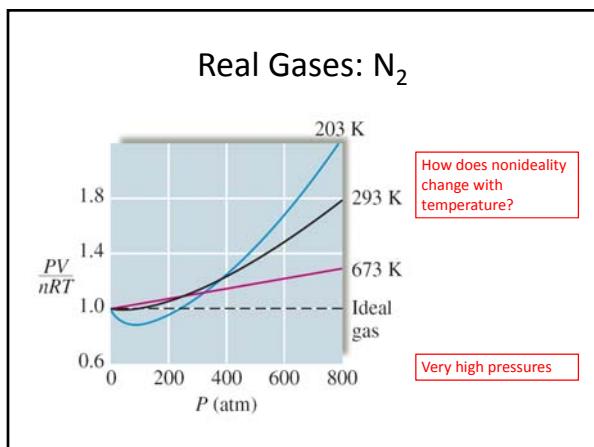
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### Real Gases: van der Waals

$$P = \frac{nRT}{V} \quad (\text{for ideal case})$$

*b* represents the volume unavailable due to volume of the actual molecules. It is a *molar* quantity. For example, for N<sub>2</sub> it is 0.0391 L/mol

How do we expect *b* to vary from gas to gas?

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### Real Gases: van der Waals

$$PV = nRT \quad (\text{for ideal case})$$

$$P' = \frac{nRT}{V-nb} \quad (\text{correctio n : measured } V \text{ is too large})$$

$P'$  would be observed if molecules have volume but are noninteracting.

Real molecules attract each other, giving lower pressure.

$P_{obs} < P'$ , and we introduce a correction factor

$$P_{obs} = P' - P''$$

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### Real Gases: van der Waals

$$PV = nRT \quad (\text{for ideal case})$$

$$P' = \frac{nRT}{V-nb} \quad (\text{correctio n : measured } V \text{ is too large})$$

$$P_{obs} = P' - P''$$

Correction factor  $P''$  is proportional to the square of the molecule density, because the number of collisions is thusly proportional:

$$\sim (n/V)^2$$

$$P_{obs} = P' - P'' = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \quad (\text{measured } P \text{ is too small})$$

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### Real Gases: van der Waals

$$PV = nRT \quad (\text{for ideal case})$$

$$P' = \frac{nRT}{V-nb} \quad (\text{correction : measured } V \text{ is too large})$$

$$P_{obs} = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \quad (P \text{ is reduced by interactions})$$




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## Real Gases: van der Waals

$PV = nRT$  (for ideal case)

$P' = \frac{nRT}{V-nb}$  (correction : measured V is too large)

$$\left[ P_{obs} + a \left( \frac{n}{V} \right)^2 \right] (V - nb) = nRT \text{ (van der Waals)}$$

$a$  represents the pressure reduction due to attraction between the actual molecules. It is a *molar* quantity. For example, for  $N_2$  it is  $1.39 \text{ atm L}^2/\text{mol}^2$

*What magnitude is  $(n/V)^2$*

*How do we expect  $a$  to vary from gas to gas?*

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**TABLE 5.3**

Values of van der Waals Constants for Some Common Gases

Gas	$a \left( \frac{\text{atm L}^2}{\text{mol}^2} \right)$	$b \left( \frac{\text{L}}{\text{mol}} \right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H <sub>2</sub>	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
Cl <sub>2</sub>	6.49	0.0562
CO <sub>2</sub>	3.59	0.0427
CH <sub>4</sub>	2.25	0.0428
NH <sub>3</sub>	4.17	0.0371
H <sub>2</sub> O	5.46	0.0305

- Do the values support the trends we predicted?

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**TABLE 5.3**

Values of van der Waals Constants for Some Common Gases

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NH <sub>3</sub>	4.17	0.0371
H <sub>2</sub> O	5.46	0.0305

Problem 5-87

- 0.5000 mol N<sub>2</sub>
- 1.000L flask
- 25.0°C
- What is the pressure?
- Ideal: 12.24 atm
- VDW: 12.13 atm
- Difference: 0.91%

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TABLE 5.3

Values of van der Waals Constants for Some Common Gases

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CH <sub>4</sub>	2.25	0.0428
NH <sub>3</sub>	4.17	0.0371
H <sub>2</sub> O	5.46	0.0305

Problem 5-93

- Of the molecules H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>, predict which has the strongest intermolecular interactions.

- CO<sub>2</sub>

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TABLE 5.3

Values of van der Waals Constants for Some Common Gases

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CH <sub>4</sub>	2.25	0.0428
NH <sub>3</sub>	4.17	0.0371
H <sub>2</sub> O	5.46	0.0305

- What trend do you see regarding intermolecular interactions for the rare gases: He, Ne, Ar, Kr, and Xe

- The "heaviest" have the strongest interactions

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Next Week: Week 7

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