

Lecture 6 CH102 A1 (MWF 9:05 am) Spring 2018 Copyright © 2018 Dan Dill dan@bu.edu

[TP] The different of speeds,  $u_1$ ,  $u_2$ , etc., in a gas is due to ...

13% 1. collisions of gas particles with the walls of the container.

13% 2. collisions of gas particles with one another

13% 3. attractions between the particles of the gas and the particles of the walls of the container.

13% 4. attractions between the particles of the gas.

13% 5. 1 and 2

13% 6. 1 and 3

13% 7. 1, 2 and 3

13% 8. 1, 2, 3 and 4

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Response Counter

10 1

Lecture 6 CH102 A1 (MWF 9:05 am)  
Wednesday, January 31, 2018

- Review: Localized and delocalized  $\pi$  orbitals
- Review: Localized and delocalized electrons
- Kinetic molecular theory, PDF: <http://goo.gl/njf3em>

Next: Complete kinetic molecular theory; Practice with particle picture of gases; Molecular speeds and their distribution; real gases (attraction and size)

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### Localized and delocalized $\pi$ orbitals

**Localized  $\pi$  orbitals** are those MOs built from **only two AOs**, each AO on adjacent atoms. As a result, localized  $\pi$  orbitals extend over only two adjacent atoms.

**Delocalized  $\pi$  orbitals** are those MOs built from **more than two AOs**, from more than two adjacent atoms. As a result, delocalized  $\pi$  orbitals extend over more than two adjacent atoms.

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### Localized and delocalized electrons

A **localized electron** is in an orbital that has 0 density between adjacent atoms.

A **delocalized electron** is in an orbital that has non-zero density between adjacent atoms.

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## Localized and delocalized electrons

An electron is **localized on an atom** if it is ...

in a  **$\sigma$  framework non-bonding orbital**, or

in a  **$\pi$  framework orbital that has a nodal plane (or 0 amplitude) between adjacent atoms**



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## Localized and delocalized electrons

Example of electrons in a  **$\sigma$  framework non-bonding orbital**:

In formate,  $\text{HC(O)O}^-$ , the two  $\text{sp}^2$  non-bonding AOs on each O atom each contain two electrons and so there are **4  $\sigma$  framework electrons** localized on the O atom.



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## Localized and delocalized electrons

Example of electrons  **$\pi$  framework orbital that has a nodal plane (or 0 amplitude) between adjacent atoms**:

In formate,  $\text{HC(O)O}^-$ , the  $\pi^n$  orbital has a nodal plane between the two atoms (and 0 amplitude on the C atom) and so **1 electron** of the two electrons it contains is **localized** on each O atom.

The  $\pi$  (bonding) orbital **does not have** a nodal plane, and so the two electrons it contains are spread among O-C-O atoms, rather than being localized on each atom.

This was the error I made in A1 lecture 5 on Monday, January 29.



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## Localized and delocalized electrons

Therefore in formate,  $\text{HC(O)O}^-$ , there are a total of **5 electrons** (4 in the  $\sigma$  framework + 1 in the  $\pi$  framework) localized on each O atom.



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**[TP]** In carbonic acid,  $\text{H}_2\text{CO}_3$ , how many electrons are localized on the terminal O atom?

0% 1. 0  
0% 2. 1  
0% 3. 2  
0% 4. 3  
0% 5. 4  
0% 6. 5  
0% 7. 6  
0% 8. 7  
0% 9. 8

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**[TP]** In carbonic acid,  $\text{H}_2\text{CO}_3$ , how many electrons are localized on the C atom?

1. 0  
2. 1  
3. 2  
4. 3  
5. 4  
6. 5  
7. 6  
8. 7  
9. 8

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### Kinetic-molecular theory of gases

**Goal:** Get microscopic expression for pressure  $P$

**Key idea 1:** Pressure is due to force exerted by particles during collisions with the container walls

**Key idea 2:** Force is due to momentum change in collision with the container walls.

**Note:** Here **upper-case**  $P$  is used for pressure and **lower-case**  $p$  is used for momentum.

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### Kinetic-molecular theory of gases

Force due to  $j^{\text{th}}$  particle of mass  $m$  and speed  $u_j$

$\Delta p = 2mu_j$  (elastic collision)

$\Delta t = 2L/u_j$  (travel to opposite wall and back)

$F = \Delta p / \Delta t = mu_j^2 / L$

Pressure due to  $j^{\text{th}}$  particle of mass  $m$  and speed  $u_j$

$$P_j = \frac{F}{\text{area}} = \frac{F}{L^2} = \frac{mu_j^2}{L^3} = \frac{mu_j^2}{V}$$

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