

Lecture 7 CH102 A1 (MWF 9:05 am) Spring 2019 Copyright © 2019 Dan Dill dan@bu.edu

**[TP]** Predict the effect of intermolecular attraction on the pressure exerted by a gaseous molecule in a collision with the wall of its container. The stronger the attraction, the ...

20% 1. greater the pressure  
 20% 2. smaller the pressure  
 20% 3. The pressure will not be affected  
 20% 4. Cannot answer without knowing the temperature  
 20% 5. Cannot answer without knowing the polarity of the molecule

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 Wednesday, February 6, 2019

- Review: Maxwell-Boltzmann distribution: CDF <https://goo.gl/VkRrsg>
- Real gases: Effect of molecular attraction
- Real gases: Effect of molecular size

Next: van der Waals equation; Phase diagrams

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### Distribution of molecular speeds

The resulting distribution, known as the Maxwell-Boltzmann (MB) distribution.

For a given  $u_{rms}$  it is always the same.

CDF <https://goo.gl/gzgjQE>

Maxwell-Boltzmann speed distribution

$M_1$ , g/mol

$T_1$ , K

$M_2$ , g/mol

$T_2$ , K

fraction

$M_1 = 32$  g/mol,  $T_1 = 300$  K  
 $ms_1 = 484$  m/s

$M_2 = 2$  g/mol,  $T_2 = 1200$  K  
 $ms_2 = 3569$  m/s

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### Effect of intermolecular attraction

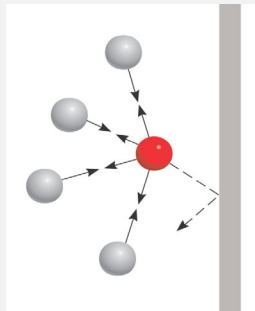
Gas particles **attract one another**: van der Waals  $a$

# hitting wall  $\propto \frac{n}{V}$

# pulling back  $\propto \frac{n}{V}$

combined effect  $\propto \left(\frac{n}{V}\right)^2$

$p_{\text{observed}} = p_{\text{ideal}} - a\left(\frac{n}{V}\right)^2$



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## Energy density and molecular attractions

We have seen that we can interpret pressure as  $\frac{\text{energy}}{\text{volume}}$ ,  $1 \text{ Pa} = 1 \text{ J/m}^3$

Let's apply this interpretation to

$$p_{\text{observed}} = p_{\text{ideal}} - a \left(\frac{n}{V}\right)^2$$

$p_{\text{ideal}} = nRT/V$  is just the **kinetic energy density** (kinetic energy per unit volume) of the ideal gas.

Similarly,  $-a \left(\frac{n}{V}\right)^2$  is the corresponding **potential energy density** of the gas due to the interpartical interactions.



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## Contributions to van der Waals a

Van der Waals  $a$  reflects intermolecular attractions present when gas particles **encounter one another**.

The larger the intermolecular attraction, the larger the numerical value of  $a$ .

Intermolecular attractions are due to the combined effect of (lectures 17 and 18, CH101 Fall 2018) ...

Hydrogen bonding (typically strongest)

Dipole-dipole interactions (can be attractive and repulsive)

Dispersion forces (always attractive)



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[TP] Predict the effect of intermolecular attraction on the pressure exerted by a gaseous molecule in a collision with the wall of its container. The stronger the attraction, the ...

- 20% 1. greater the pressure
- 20% 2. smaller the pressure
- 20% 3. The pressure will not be affected
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- 20% 5. Cannot answer without knowing the polarity of the molecule

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[TP] Equal amounts of gases A and C are in a single container. The molar masses of the **gases are identical**, but gas C has **stronger intermolecular forces**. The container is pierced with a hole **0.003 mm** in diameter. After 5 minutes, the container will contain ...

- 33% 1. more A than C
- 33% 2. the same amount of A and C
- 33% 3. more C than A

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**[Group quiz]** Which of the following is the correct order of species for increasing value of **van der Waals  $a$** ? (See lectures 17 and 18, CH101 Fall 2018).

- 20% 1.  $H_2 < Kr < CO_2 < H_2O$   
 20% 2.  $H_2 < Kr < H_2O < CO_2$   
 20% 3.  $Kr < H_2 < CO_2 < H_2O$   
 20% 4.  $Kr < H_2 < H_2O < CO_2$   
 20% 5.  $H_2 < H_2O < Kr < CO_2$



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## Contributions to van der Waals $a$

Van der Waals  $a$  reflects intermolecular attractions present when gas particles **encounter one another**.

Therefore, hydrogen bonding **can** make a contribution.



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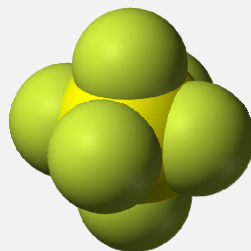
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## Effect of molecular size

While gas particles are tiny compared to the volume of their container, they do **take up some space**.

The graphic illustrates the **electron cloud of  $SF_6$** .



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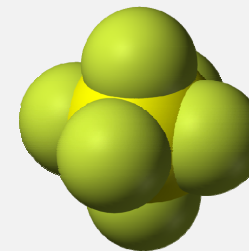
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## Effect of molecular size

Gas particles **have a volume**: van der Waals  $b$

$$V_{\text{container}} = V_{\text{empty}} + bn$$

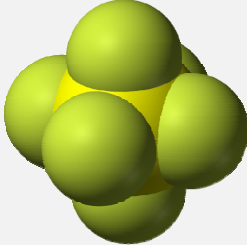


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[TP] Gas particles **have a volume** measured by van der Waals  $b$ .  
For  $\text{SF}_6$ ,  $b = 88 \text{ mL/mol}$ . The percent of gas **container volume** taken up by the  $\text{SF}_6$  molecules themselves is ...

17% 1. 0.01%  
17% 2. 0.05%  
17% 3. 0.1%  
17% 4. 0.5%  
17% 5. 1%  
17% 6. 5%



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### Effect of molecular size

Gas particles **have a volume**: van der Waals  $b$   
 $V = V_{\text{container}} = V_{\text{empty}} + bn$

For  $\text{SF}_6$ ,  $b = 88 \text{ mL/mol}$   
% of molar gas volume ...  
 $\approx (0.088 / 22) \times 100\% = 0.40\%$

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### A gas law for “real” gases: van der Waals equation

We know the ideal gas law  $pV = nRT$  where  $p$  **does not** account for inter-particle attractions ...

$$p = p_{\text{ideal}} = p_{\text{observed}} + a \left( \frac{n}{V_{\text{container}}} \right)^2$$

and  $V$  **does not** account for particle volume ...

$$V = V_{\text{empty}} = V_{\text{container}} - bn$$

Combine these two expressions into an equation relating  $p_{\text{observed}}$ ,  $V_{\text{container}}$ , and  $T$ .

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