# **GENERAL PHYSICS PH1110**

Nam Le, Dr.

School of Engineering Physics Hanoi University of Science and Technology

# 2. THERMODYNAMICS

#### 2.4 REAL GASES

1 Van der Waals equation of state

2 Experimental isotherms

- 1. Van der Waals equation of state
- From ideal gases to real gases

- From ideal gases to real gases
  - The ideal gas law treats gas molecules as point particles

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

• The space that the ideal gas molecules can move freely is equal to  $V_m$ .

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

• The space that the ideal gas molecules can move freely is equal to  $V_{\rm m}$ . For a real gas, however, it is smaller than  $V_{\rm m}$ 

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

• The space that the ideal gas molecules can move freely is equal to  $V_{\rm m}$ . For a real gas, however, it is smaller than  $V_{\rm m}$  because the molecules occupy some space.

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

- The space that the ideal gas molecules can move freely is equal to  $V_{\rm m}$ . For a real gas, however, it is smaller than  $V_{\rm m}$  because the molecules occupy some space.
- To account for the volume that real gas molecules take up,

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

- The space that the ideal gas molecules can move freely is equal to  $V_{\rm m}$ . For a real gas, however, it is smaller than  $V_{\rm m}$  because the molecules occupy some space.
- To account for the volume that real gas molecules take up, van der Waals replaced  $V_{\rm m}$  by  $(V_{\rm m}-b)$ ,

- From ideal gases to real gases
  - The <u>ideal gas law</u> treats gas molecules as point particles that do not interact with each other.

$$pV_{\rm m} = RT$$
 ( $V_{\rm m}$  is the molar volume)

- The space that the ideal gas molecules can move freely is equal to  $V_{\rm m}$ . For a real gas, however, it is smaller than  $V_{\rm m}$  because the molecules occupy some space.
- To account for the volume that real gas molecules take up, van der Waals replaced  $V_{\rm m}$  by  $(V_{\rm m}-b)$ , where b is the volume occupied by molecules of one mole.

• The second modification comes from the fact that the real gas molecules **do** interact with each other.

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.
- Therefore, if *p* is the observed pressure,

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.
- Therefore, if *p* is the observed pressure, the pressure in the equation of state should be greater than *p*.

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.
- Therefore, if *p* is the observed pressure, the pressure in the equation of state should be greater than *p*.
- Van der Waals added to the observed pressure p a term  $a/V_{\rm m}^2$ , where a is a constant whose value depends on the gas.

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.
- Therefore, if *p* is the observed pressure, the pressure in the equation of state should be greater than *p*.
- Van der Waals added to the observed pressure p a term  $a/V_{\rm m}^2$ , where a is a constant whose value depends on the gas.
  - ▶ The term added is inversely proportional to the square the volume

- The second modification comes from the fact that the real gas molecules **do** interact with each other.
- The attraction between molecules leads to a decrease in the pressure of the real gas as compared to that of the ideal gas.
- Therefore, if *p* is the observed pressure, the pressure in the equation of state should be greater than *p*.
- Van der Waals added to the observed pressure p a term  $a/V_{\rm m}^2$ , where a is a constant whose value depends on the gas.
  - ▶ The term added is inversely proportional to the square the volume since the average force between molecules is directly proportional to the square of the density of molecules.

• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

$$pV_{\rm m} = RT$$

• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

$$\boxed{pV_{\rm m} = RT} \implies \left(p + \frac{a}{V_{\rm m}^2}\right)(V_{\rm m} - b) = RT$$

• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

$$\boxed{pV_{\rm m} = RT} \qquad \Longrightarrow \qquad \left| \left( p + \frac{a}{V_{\rm m}^2} \right) (V_{\rm m} - b) = RT \right|$$

• For an arbitrary amount of gas:

• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

$$\boxed{pV_{\rm m} = RT} \qquad \Longrightarrow \qquad \left| \left( p + \frac{a}{V_{\rm m}^2} \right) (V_{\rm m} - b) = RT \right|$$

• For an arbitrary amount of gas:

$$V_{\rm m} \rightarrow \frac{\mu}{m} V$$

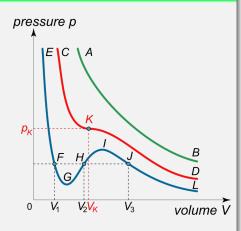
• So, according to van der Waals, the EOS for real gases can be obtained from the EOS for ideal gases by replacing:

$$V_{\rm m} \rightarrow (V_{\rm m} - b), \qquad p \rightarrow \left(p + \frac{a}{V_{\rm m}^2}\right)$$

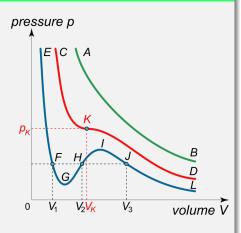
$$\boxed{pV_{\rm m} = RT} \qquad \Longrightarrow \qquad \boxed{\left(p + \frac{a}{V_{\rm m}^2}\right)(V_{\rm m} - b) = RT}$$

• For an arbitrary amount of gas:

$$V_{\rm m} \rightarrow \frac{\mu}{m} V \Longrightarrow \left[ \left( p + \frac{m^2}{\mu^2} \frac{a}{V^2} \right) (V - \frac{m}{\mu} b) = \frac{m}{\mu} RT \right]$$

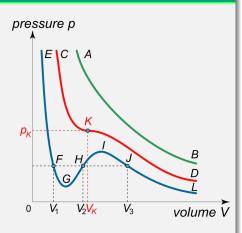


- Van der Waals isotherms
  - At very high temperature,

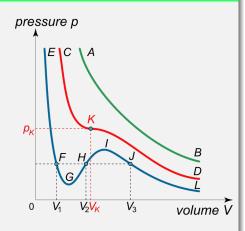


#### Van der Waals isotherms

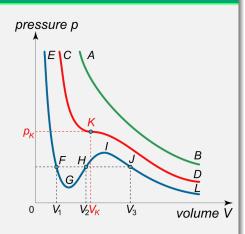
• At very high temperature, the isotherm is similar to that of an ideal gas.



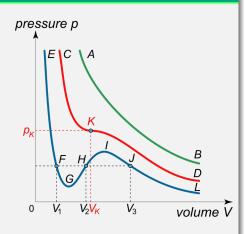
- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature  $T_c$ ,



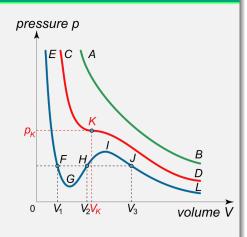
- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature T<sub>c</sub>, it has an inflection point



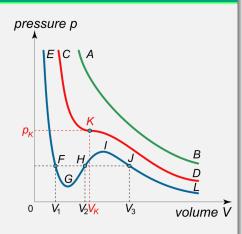
- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature T<sub>c</sub>, it has an inflection point (the critical point K in the red curve).



- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature T<sub>c</sub>, it has an inflection point (the critical point K in the red curve).
- Below  $T_c$ ,

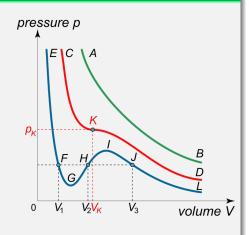


- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature T<sub>c</sub>, it has an inflection point (the critical point K in the red curve).
- Below  $T_c$ , it is very different from an ideal gas isotherm.



#### Van der Waals isotherms

- At very high temperature, the isotherm is similar to that of an ideal gas.
- At temperature T<sub>c</sub>, it has an inflection point (the critical point K in the red curve).
- Below  $T_c$ , it is very different from an ideal gas isotherm.



#### Exercise

• For one mole of a real gas at critical point, find its volume, temperature and pressure in terms of *a*, *b* and *R*.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \Longrightarrow \qquad p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\frac{\partial p}{\partial V} =$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3},$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \qquad \frac{\partial^2 p}{\partial V^2} =$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \qquad \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

• Van der Waals equation for one mole  $(V \equiv V_m)$ :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \qquad \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

• At critical point:

• Van der Waals equation for one mole  $(V \equiv V_m)$ :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \Longrightarrow \qquad p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3}, \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}$$

• At critical point:

$$p_{\rm c} = \frac{RT_{\rm c}}{V_{\rm c} - b} - \frac{a}{V_{\rm c}^2}, \quad -\frac{RT_{\rm c}}{(V_{\rm c} - b)^2} + \frac{2a}{V_{\rm c}^3} = 0, \quad \frac{2RT_{\rm c}}{(V_{\rm c} - b)^3} - \frac{6a}{V_{\rm c}^4} = 0$$

• Van der Waals equation for one mole  $(V \equiv V_m)$ :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \Longrightarrow \qquad p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3}, \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}$$

• At critical point:

$$p_{\rm c} = \frac{RT_{\rm c}}{V_{\rm c} - b} - \frac{a}{V_{\rm c}^2}, \quad -\frac{RT_{\rm c}}{(V_{\rm c} - b)^2} + \frac{2a}{V_{\rm c}^3} = 0, \quad \frac{2RT_{\rm c}}{(V_{\rm c} - b)^3} - \frac{6a}{V_{\rm c}^4} = 0$$

• Solutions:

• Van der Waals equation for one mole  $(V \equiv V_m)$ :

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
  $\Longrightarrow$   $p = \frac{RT}{V - b} - \frac{a}{V^2}$ 

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \qquad \qquad \frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

• At critical point:

$$p_{\rm c} = \frac{RT_{\rm c}}{V_{\rm c} - b} - \frac{a}{V_{\rm c}^2}, \quad -\frac{RT_{\rm c}}{(V_{\rm c} - b)^2} + \frac{2a}{V_{\rm c}^3} = 0, \quad \frac{2RT_{\rm c}}{(V_{\rm c} - b)^3} - \frac{6a}{V_{\rm c}^4} = 0$$

• Solutions:

$$V_{\rm c} = 3b$$

$$T_{\rm c} = \frac{8a}{27bR}$$

$$p_{\rm c} = \frac{a}{27b^2}$$

# 2. THERMODYNAMICS

#### 2.4 REAL GASES

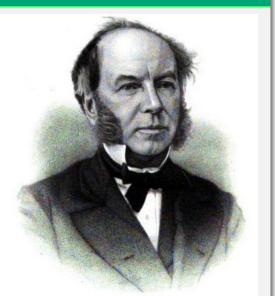
1 Van der Waals equation of state

#### **Thermodynamics** ⊳ Real gases

# 2. Experimental isotherms

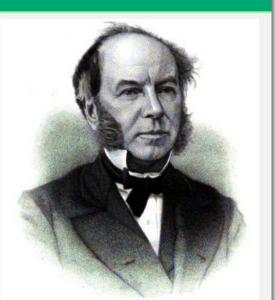
Thomas Andrews was an Irish chemist and physicist.

Thomas Andrews was an Irish chemist and physicist.



Thomas Andrews was an Irish chemist and physicist.

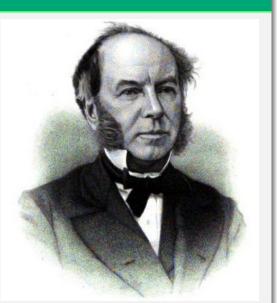
He experimentally studied isothermal processes of carbon dioxide in 1863.



Thomas Andrews was an Irish chemist and physicist.

He experimentally studied isothermal processes of carbon dioxide in 1863.

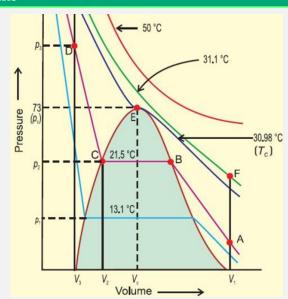
He did experiments with  $1.0 \,\text{mol}$  of  $\text{CO}_2$ .



Thomas Andrews was an Irish chemist and physicist.

He experimentally studied isothermal processes of carbon dioxide in 1863.

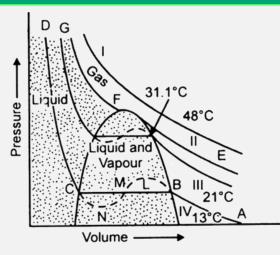
He did experiments with 1.0 mol of CO<sub>2</sub>.



Thomas Andrews was an Irish chemist and physicist.

He experimentally studied isothermal processes of carbon dioxide in 1863.

He did experiments with 1.0 mol of  $CO_2$ .



• The critical temperature of CO<sub>2</sub> is  $T_c = 31$  °C.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium. On the left of this range is solid, and on the right is gas.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium. On the left of this range is solid, and on the right is gas.
- The critical isotherm is flat at one point only.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium. On the left of this range is solid, and on the right is gas.
- The critical isotherm is flat at one point only.
- Self-study

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium. On the left of this range is solid, and on the right is gas.
- The critical isotherm is flat at one point only.
- Self-study
  - Van der Waals isotherms vs. Andrews isotherms.

- The critical temperature of  $CO_2$  is  $T_c = 31$  °C.
- Above  $T_c$ ,  $CO_2$  can only exist in the gaseous state. The isotherms are similar to those of ideal gases.
- Below  $T_c$ , the isotherms is flat over a range of volume. Liquid and vapor coexist in this range, in dynamic equilibrium. On the left of this range is solid, and on the right is gas.
- The critical isotherm is flat at one point only.
- Self-study
  - Van der Waals isotherms vs. Andrews isotherms.
  - Joule-Thomson effect