Ministry of Higher Education and Scientific Research
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Department of Biochemistry

Physical chemistry

Lecture 5

Real Gases and Van Der Waal Equation

By

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Real gases

Real gases do not obey the perfect gas law exactly because molecules interact with each other. Two important intermolecular forces exist: repulsive forces attractive forces.

1.4 Molecular interactions

1.5 The van de Waals equation

1.6 The principle of corresponding states

1.4 Molecular interactions

Repulsive forces between molecules assist expansion and attractive forces assist compression. They are significant only when molecules are almost in contact: short-range interactions.

Attractive forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching. Attractive forces are ineffective when the molecules are far apart.

1.4 Molecular interactions

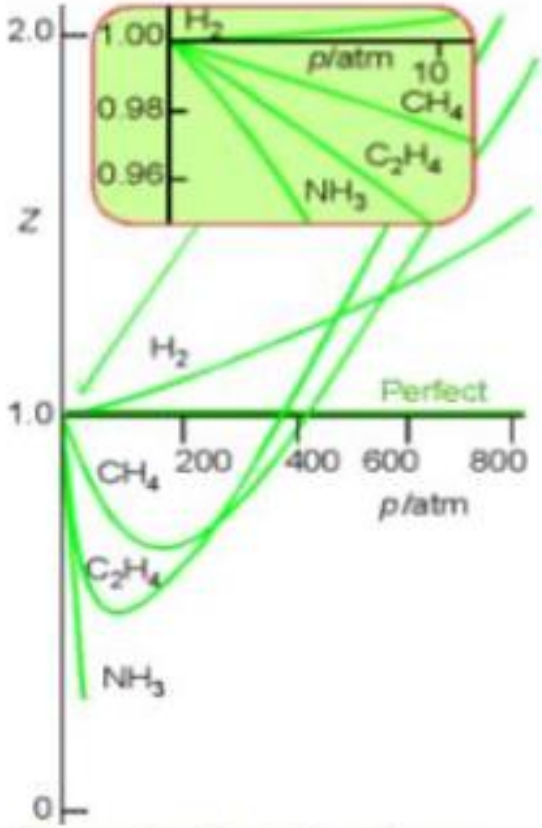
1). The compression factor

The compression factor, *Z*, is defined as

$$pV_m = ZRT \qquad Z = \frac{pV_m}{RT}$$

For a perfect gas, *Z* = 1 under all conditions; the deviation of *Z* from 1 is a measure of departure from perfect behaviour.

1.4 Molecular interactions



Results by plotting the compression factor, Z, against pressure for several gases at 0 °C.

At very low pressures: Z □ 1.

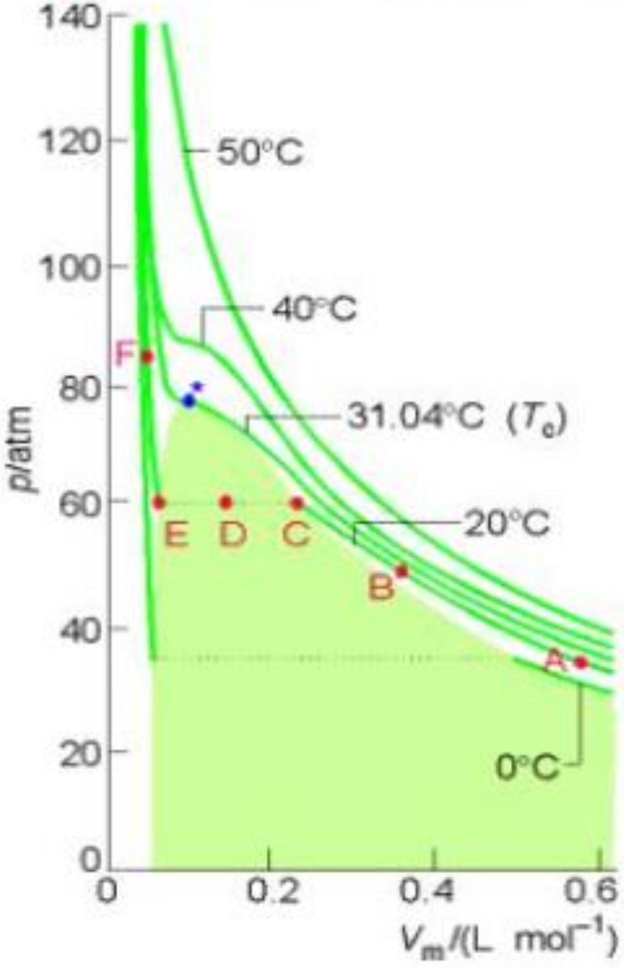
At high pressures: Z> 1.
Repulsive forces are now dominant.

At intermediate pressures: Z<1
For most gases have, the attractive forces are dominant. .

A perfect gas has Z = 1 at all pressures.

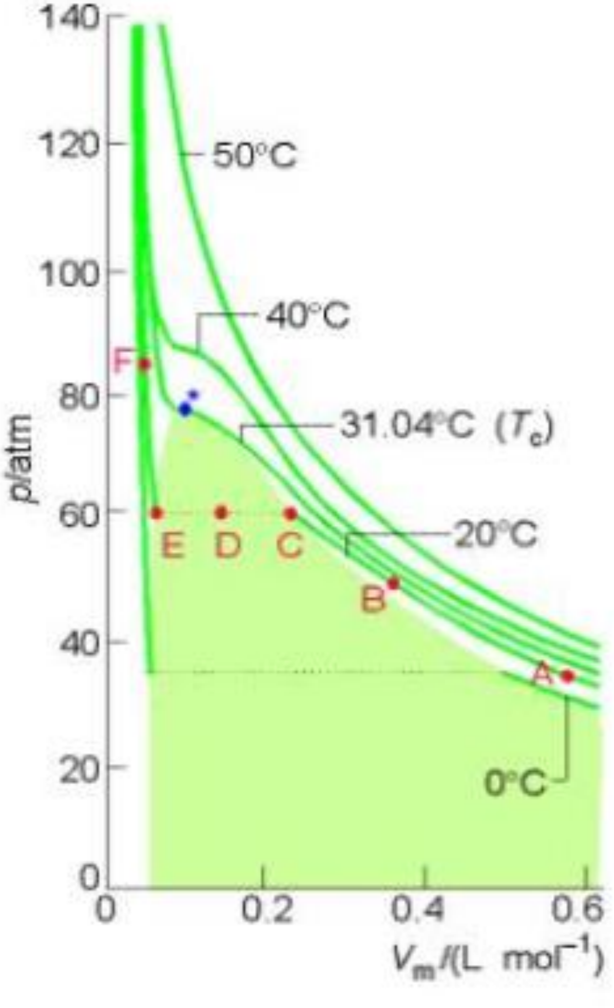
1.4 Molecular interactions

2). Virial coefficients



At large molar volumes and high temperatures the real isotherms do not differ greatly from perfect isotherms. The small differences suggest that the perfect gas law is in fact the first term in the expression of the form:

1.4 Molecular interactions



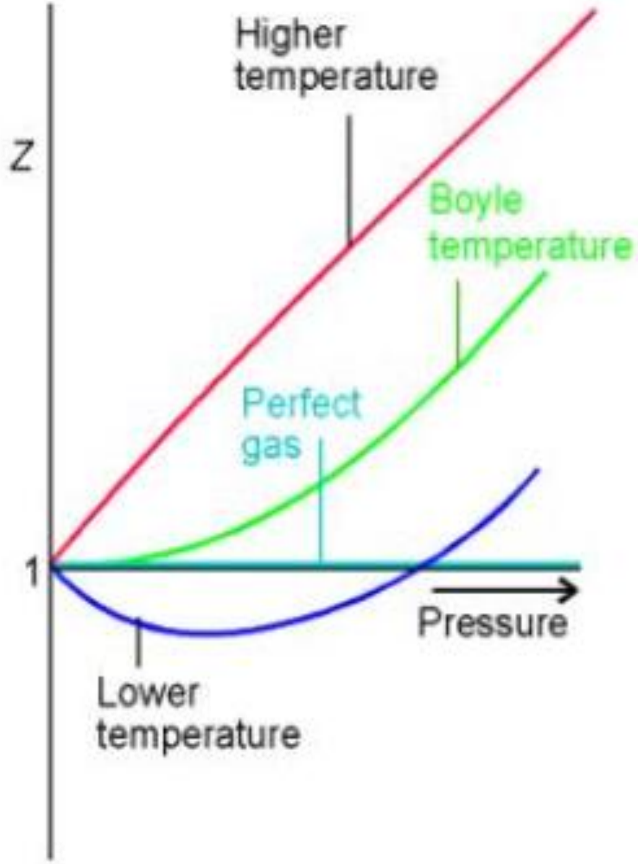
$$pV_m = RT(1 + B'p + C'p^2 + \cdots)$$

$$pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots\right)$$

These are two versions of the virial equation of state. The coefficients *B*, *C*,…, which depend on the *T*, are the second, third,… virial coefficients; the first virial coefficient is 1.

1.4 Molecular interactions

Boyle Temperature, T_B



$(\partial Z/\partial p)_{T,P\to 0} > 0$ At higher T

$(\partial Z/\partial p)_{T,P\to 0} < 0$ At lower T

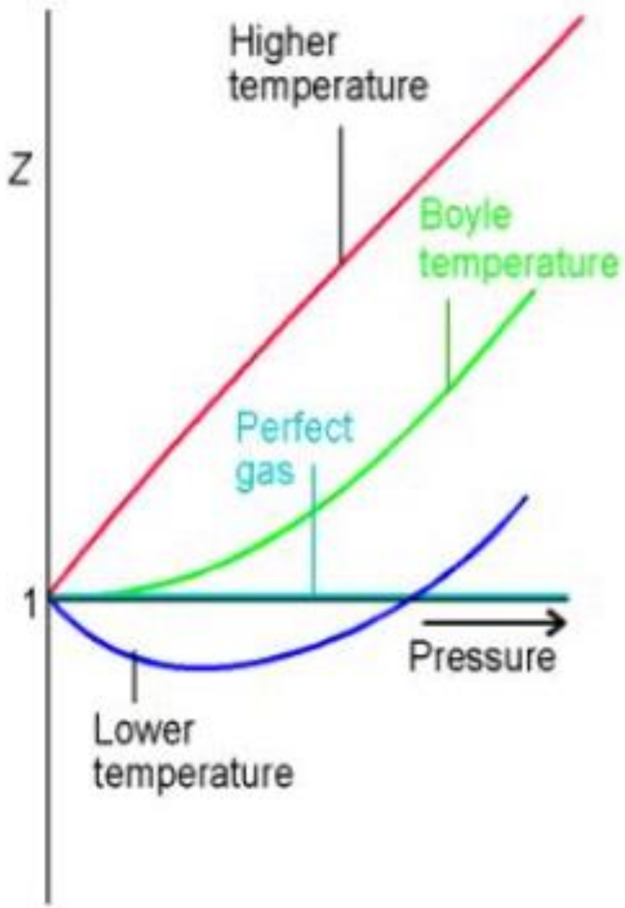
$(\partial Z/\partial p)_{T,P\to 0} = 0$ At T_B

$(\partial pV_m/\partial p)_{T,P\to 0} = 0$ At T_B

T_B is so called the Boyle Temperature

1.4 Molecular interactions

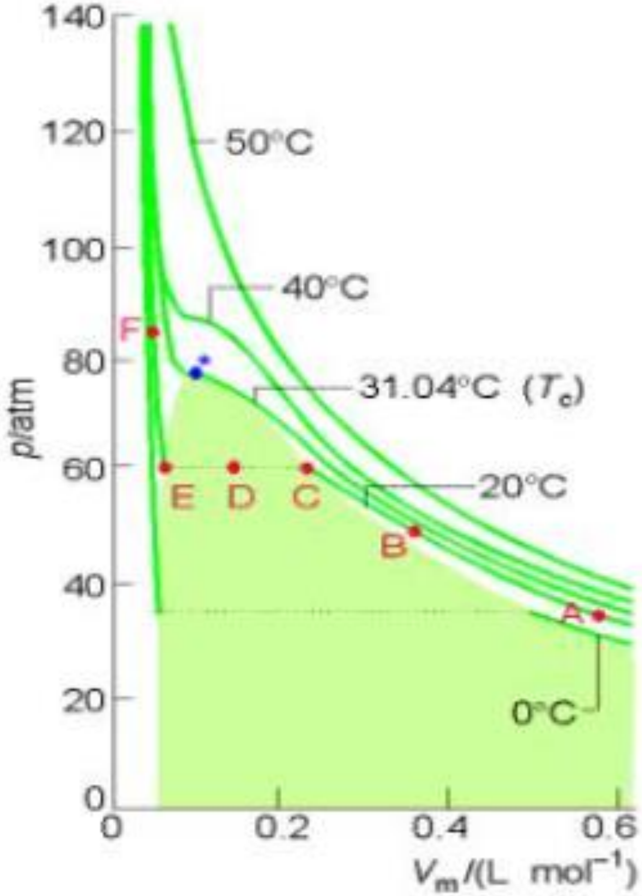
Boyle Temperature, T_B



At Boyle temperature, T_B the properties of the real gas coincide with those of a perfect gas as p □ 0; and pV_m□ $R\ T_B$

1.4 Molecular interactions

3). Condensation



Experimental isotherms of carbon dioxide at several temperatures

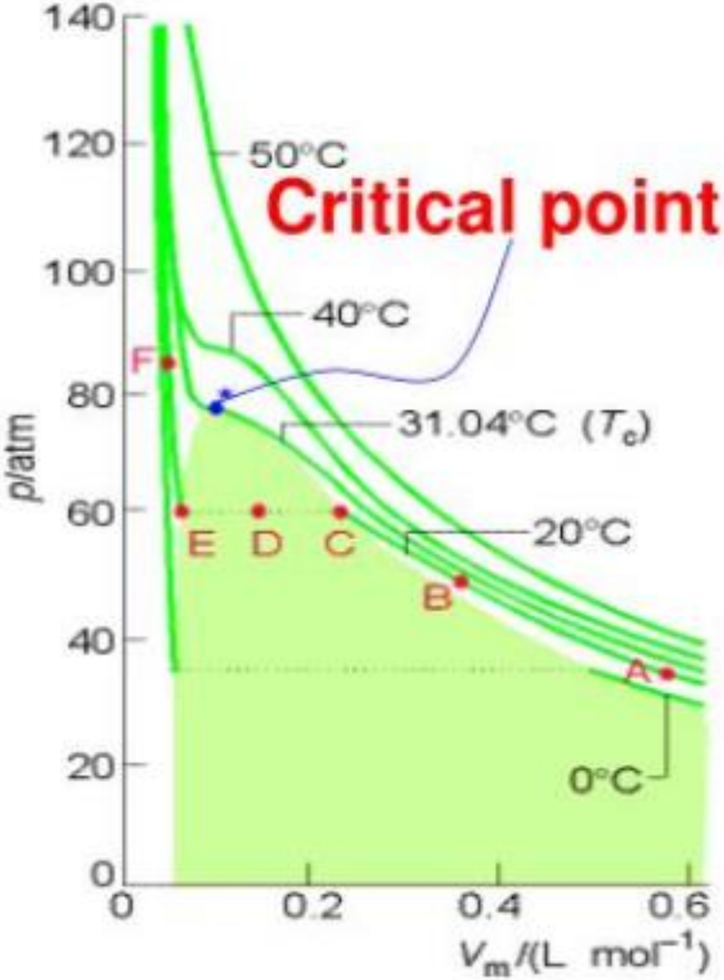
At C, all similarity to perfect behaviour is lost. This stage is represented by the horizontal line CDE. At the point just to the left of C, a liquid appears, and there are two phases in the system in this stage.

The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the vapour pressure of the liquid at the temperature of the experiment.

At E, the sample is entirely liquid.

1.4 Molecular interactions

4). Critical constants

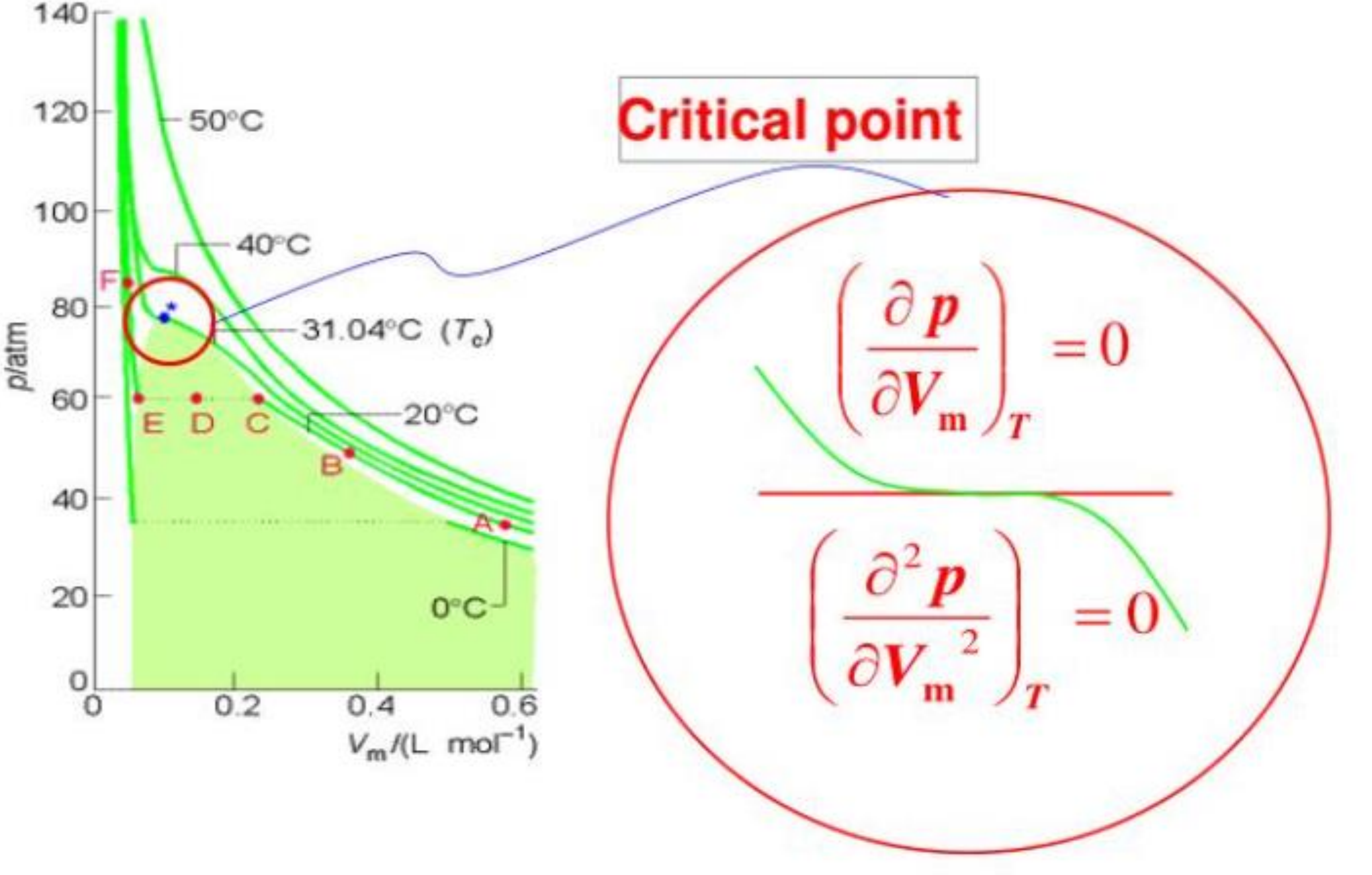


Critical point

At and above T_c, the sample has a single phase. The liquid phase of a substance does not form above the critical temperature.

T_c , the critical point of the gas. Critical constants are different from gas to gas.

1.4 Molecular interactions



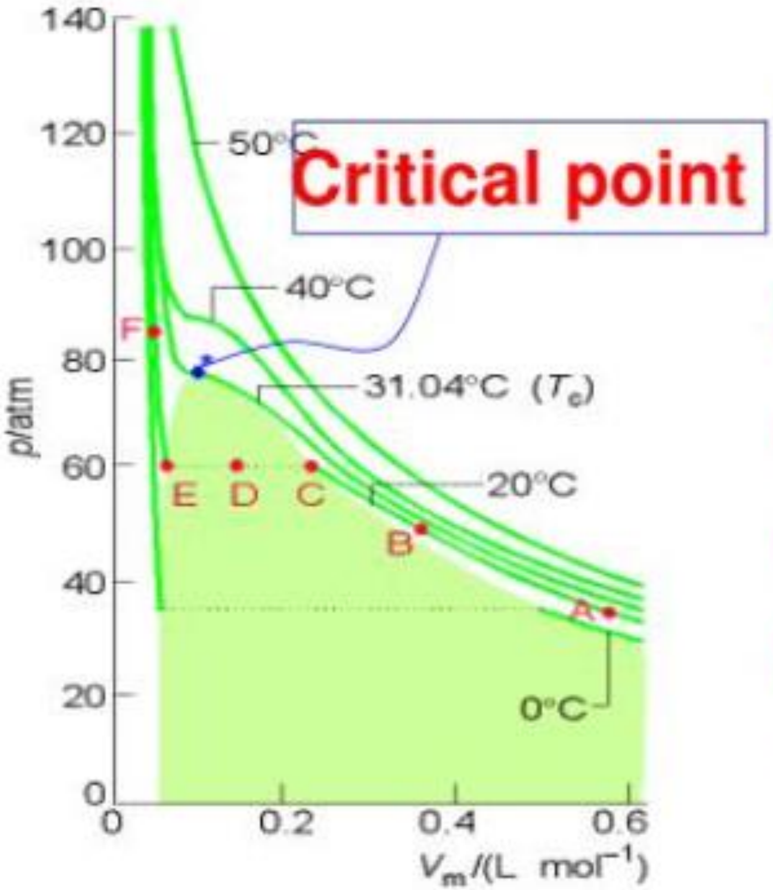
Critical point

$$\left(\frac{\partial p}{\partial V_m}\right)_T = 0$$

$$\left(\frac{\partial^2 p}{\partial V_m{}^2}\right)_T = 0$$

1.4 Molecular interactions

4). Critical constants



Critical point

The temperature, pressure, and molar volume at the critical point are called:

Critical temperature, T_c

Critical pressure, p_c

Critical molar volume, V_c

T_c, p_c, V_c -critical constants

1.5 The van der Waals equation

For the perfect gas:

1). The size of molecules is negligible;

حجم الجزيئات يمكن اهماله

2). Molecules do not interact;

الجزيئات لا تتفاعل

$$\cdot\cdot pV=nRT$$

For real gases:

1). The molecule itself occupies a volume;

الجزيئة نفسها تشغل حجما

2). There are interactions among molecules;

توجد تفاعلات بين الجزيئات

…

$$(p+\triangle p)(V-\triangle V)=nRT$$

1.5 The van der Waals equation

1). Expressions the van der Waals equation

$$(p+\triangle p)\,(V-\triangle V)=nRT$$

$$\Delta p=\frac{a}{V_{\mathrm{m}}^{2}}$$

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

$$\Delta V=b$$

$$\left(p+\frac{n^{2}a}{V^{2}}\right)(V-nb)=nRT$$

$$p=\frac{RT}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^{2}}$$

1.5 The van der Waals equation

1). Expressions the van der Waals equation

$\frac{a}{V_m^2}$, the internal pressure due to intermolecular forces.

The constants *a* and *b* are the van der Waals coefficients. They are characteristic of each gas but independent of the temperature.

1.5 The van der Waals equation

2). The features of the equation

(1) Perfect gas isotherms are obtained at high temperatures and large molar volumes.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$pV_m = RT$$

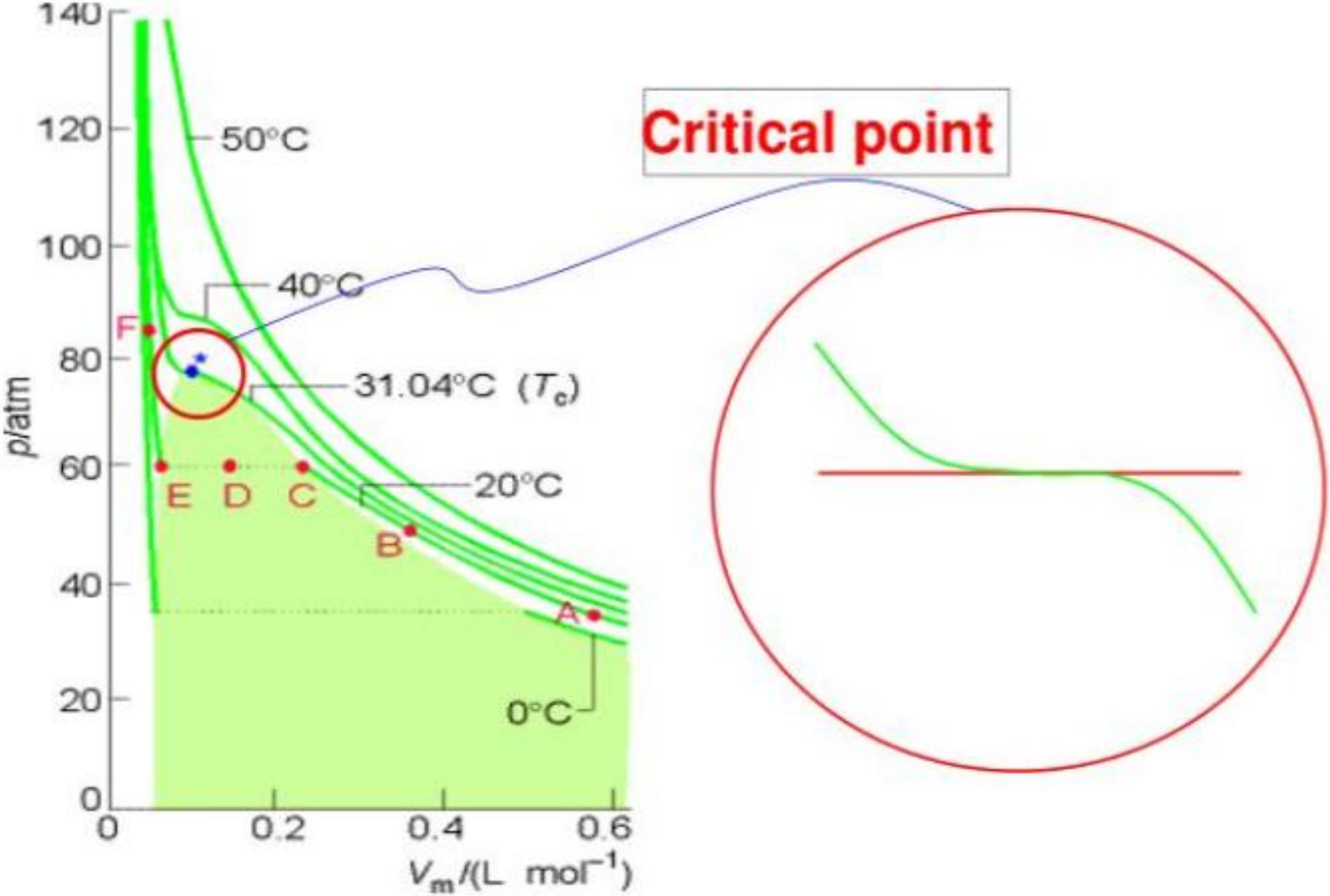
1.5 The van der Waals equation

2). The features of the equation

(2) The critical constants are related to the van der Waals coefficients.

At the critical point:

1.5 The van der Waals equation



1.5 The van der Waals equation

2). The features of the equation

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

$$p = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2}$$

$$\frac{\partial p}{\partial V_{\mathrm{m}}} = -\frac{RT}{(V_{\mathrm{m}} - b)^2} + \frac{2a}{V_{\mathrm{m}}^3} = 0 \qquad \frac{\partial^2 p}{\partial^2 V_{\mathrm{m}}} = \frac{2RT}{(V_{\mathrm{m}} - b)^3} - \frac{6a}{V_{\mathrm{m}}^4} = 0$$

1.5 The van der Waals equation

V_c	p_c	T_c	R
$V_c = 3b$	$p_c = \frac{a}{27b^2}$	$T_c = \frac{8a}{27Rb}$	$R = \frac{8p_cV_c}{3T_c}$

The critical compression factor

$$Z_c = \frac{p_cV_c}{RT_c} = \frac{3}{8} = 0.375$$

For all gases. the critical compression factor, Z_c, is constant.

Example:

Calculate the pressure of 1 mole of a real gas (nitrogen, N2) at 300 k, if the volume is 10L. Given the van der waals constants for nitrogen are:

- $a = 1.39\,\mathrm{L^2atm/mol^2}$
- $b = 0.0391\,\mathrm{L/mol}$

Solution:

1. Write down the Van der Waals equation:

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

2. Plug in the known values:

- $a = 1.39\,\mathrm{L^2atm/mol^2}$
- $b = 0.0391\,\mathrm{L/mol}$
- $R = 0.0821\,\mathrm{L\cdot atm/mol\cdot K}$
- $T = 300\,\mathrm{K}$
- $V = 10\,\mathrm{L}$
- $n = 1\,\mathrm{mol}$

Substitute into the equation:

$$\left(P + \frac{1.39}{10^2}\right)(10 - 0.0391) = 1 \times 0.0821 \times 300$$

$$\left(P + \frac{1.39}{100}\right)(9.9609) = 24.63$$

$$(P + 0.0139)\,(9.9609) = 24.63$$

$$P + 0.0139 = \frac{24.63}{9.9609}$$

$$P + 0.0139 = 2.474$$

$$P = 2.474 - 0.0139$$

$$P = 2.4601\,\mathrm{atm}$$


Thank
you