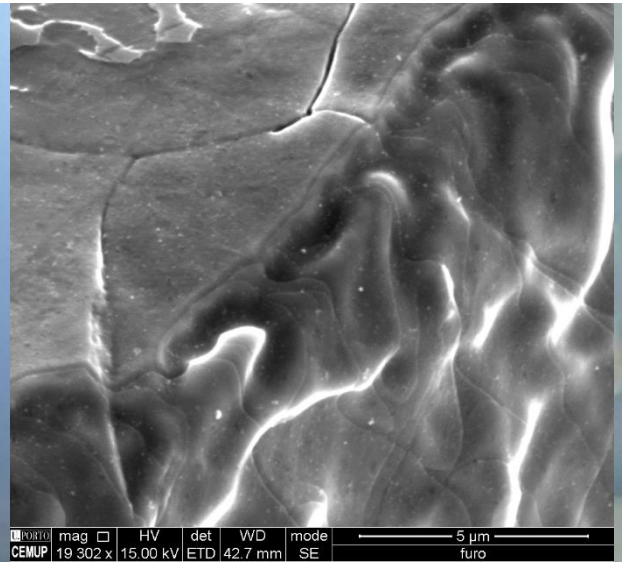
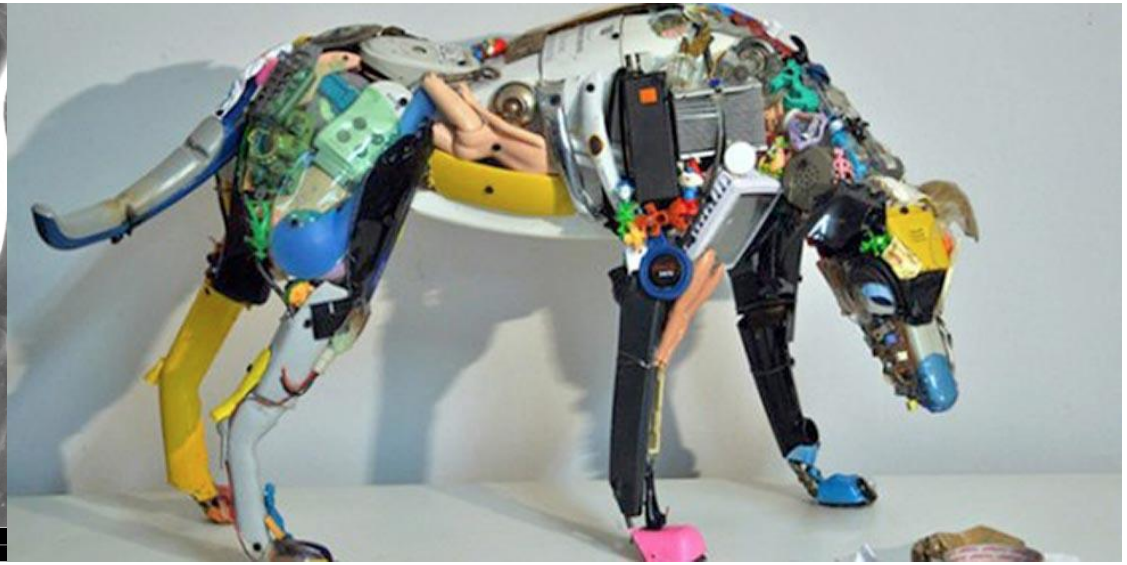
Physical Chemistry

... iremos explorar, refletir, aprender ?..

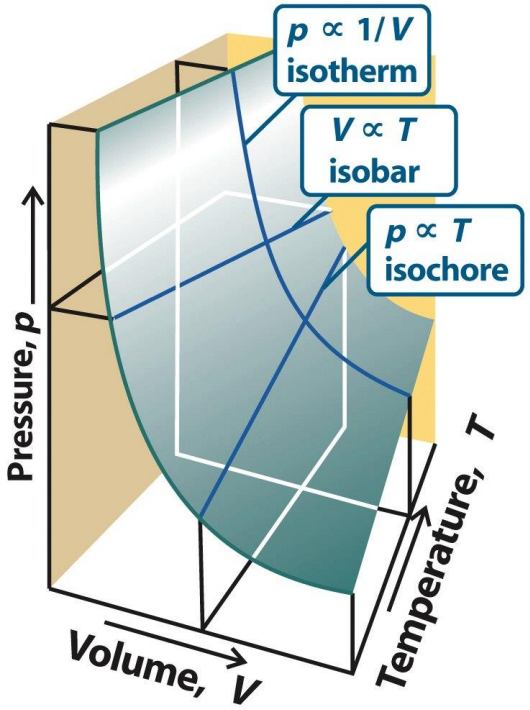
Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.





EoS | Equation of State

Properties of Gases (EoS: *p, V, T)*



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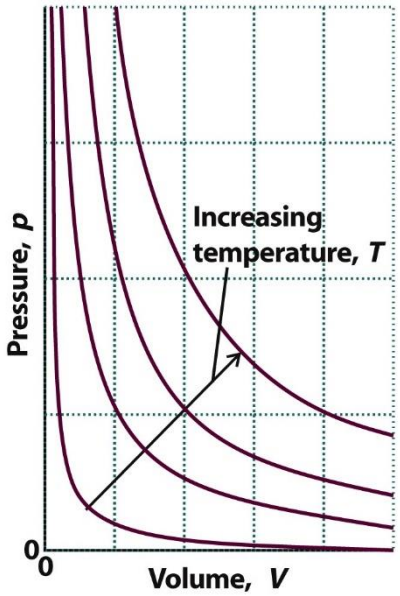

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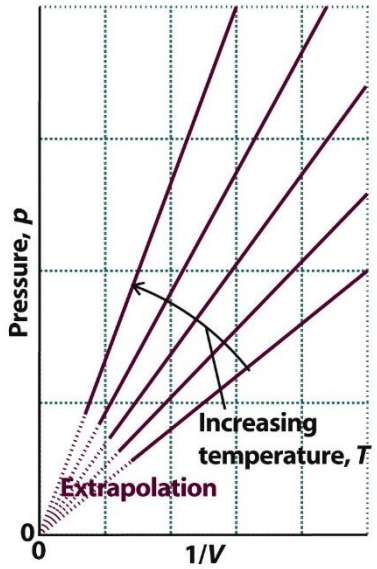

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Perfect gas

$$pV = nRT$$

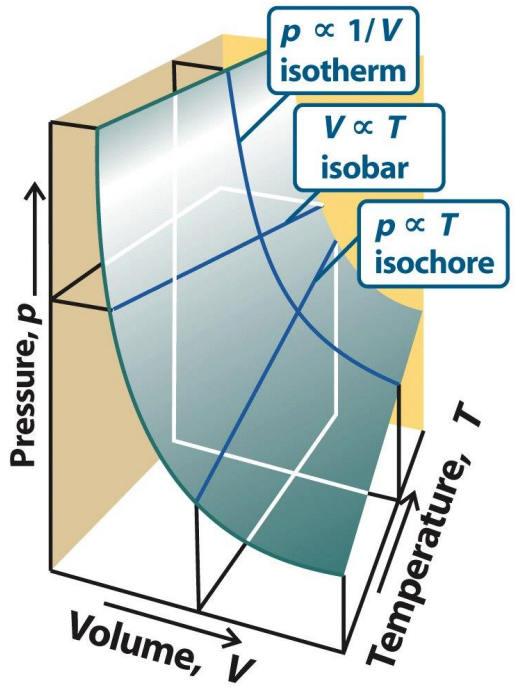
$$p = nRT.f(\frac{1}{V})$$

$$V = nRT.f(\frac{1}{p})$$

$$V_m = \frac{V}{n} = RT.f(\frac{1}{p})$$

EoS | Equation of State

Properties of Gases (EoS: *p, V, T)*



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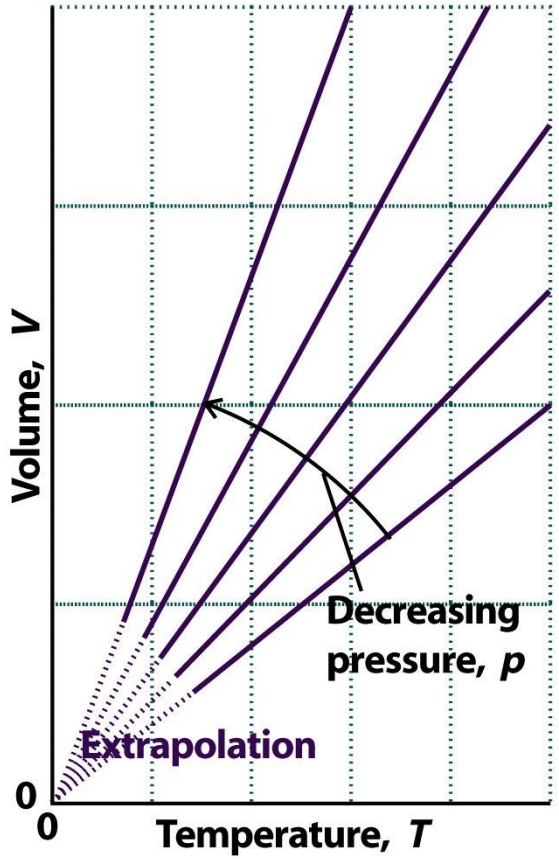

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$$V = nRT.f(\frac{1}{p})$$

Perfect gas

$$pV = nRT$$

Mixtures of gases

$$V_m = \frac{V}{n} = RT.f(\frac{1}{p})$$

Dalton Law

$$n_t = n_a + n_b + n_c + \ldots\ldots$$

$$p_t = pa + pb + p_c + \ldots\ldots$$

$$p_i = n_i RT/V$$

$$p_i = x_i n_t \frac{RT}{V} = x_i p_t$$

Table 1.3 The composition of dry air at sea level

Component	Percentage	
	By volume	By mass
Nitrogen, N_2	78.08	75.53
Oxygen, O_2	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO_2	0.031	0.047
Hydrogen, H_2	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH_4	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	1.2×10^{-5}
Ozone, O_3: summer	$7.0 \quad 10^{-6}$	$1.2 \quad 10^{-5}$
winter	$2.0 \quad 10^{-6}$	$3.3 \quad 10^{-6}$

Table 1-3
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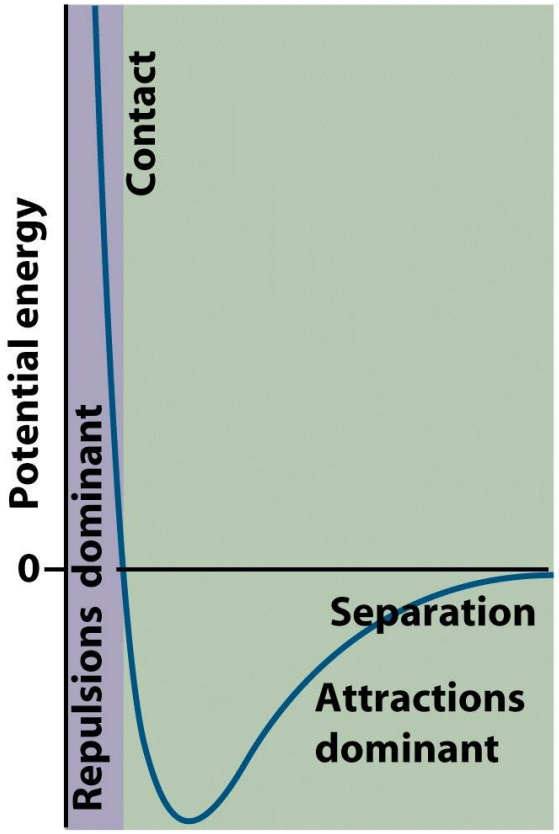
	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.780	0.210	0.0096

We have not had to assume that the gases are perfect: partial pressures are defined as $p_J = x_J p$ for any kind of gas.

Pressure equilibrium

Real gas



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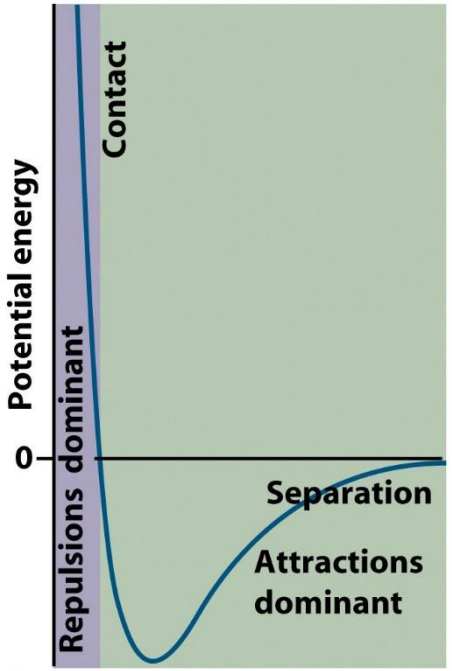
The compression factor, *Z*

$$Z = \frac{V_m}{V_m{}^0}$$

$V_m = RT/p$ (Real gas)

$$Z = \frac{RT/p}{V_m{}^0} \qquad pV_m = RT.Z$$

Pressure equilibrium



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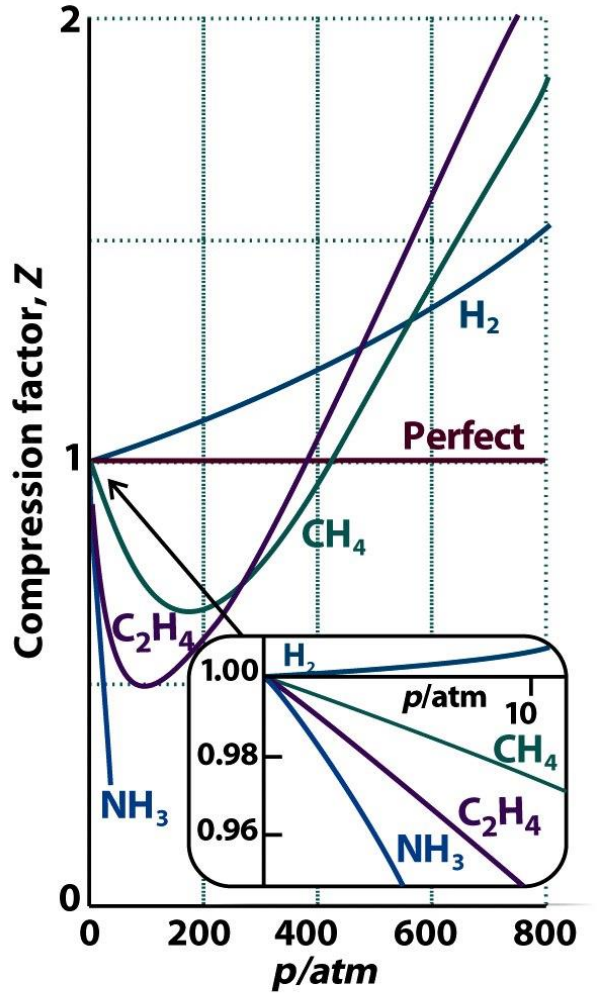

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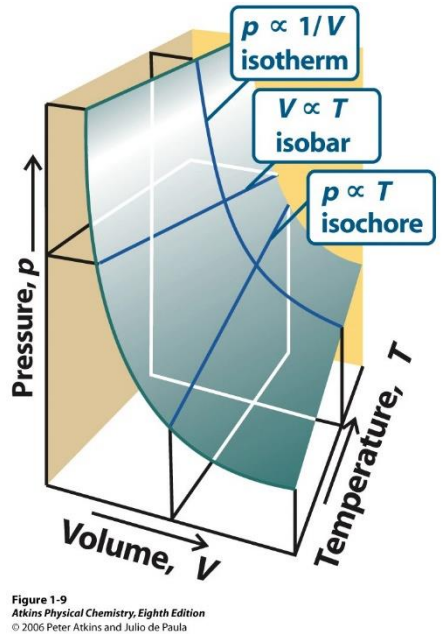
van der Waals ..equation

Approximate equation of state **EoS**
J.D. van der Waals in 1873

The **van der Waals equation** is

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

The constants a and b are called the **van der Waals coefficients.**



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van der Waals ... Equation

$$PV = n\,RT$$

R is the gas constant

P V = nRT ideal

real

$$\left(p + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT \qquad (8.25)$$

Ideal pressure

Ideal volume

Measured pressure

Correction factor to account for intermolecular attractions

Measured volume

Correction factor to account for the finite size of the molecules

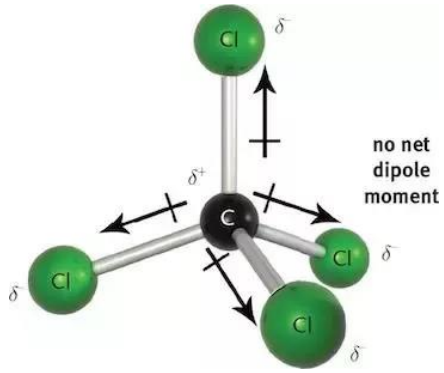
Corrects P
..intermolecular interactions
"**n**" dependence
"**V**" dependence

Corrects V
..space occupied
"**n**" dependence

Table 5.3
van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{\text{atm}\cdot\text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

CCl_4

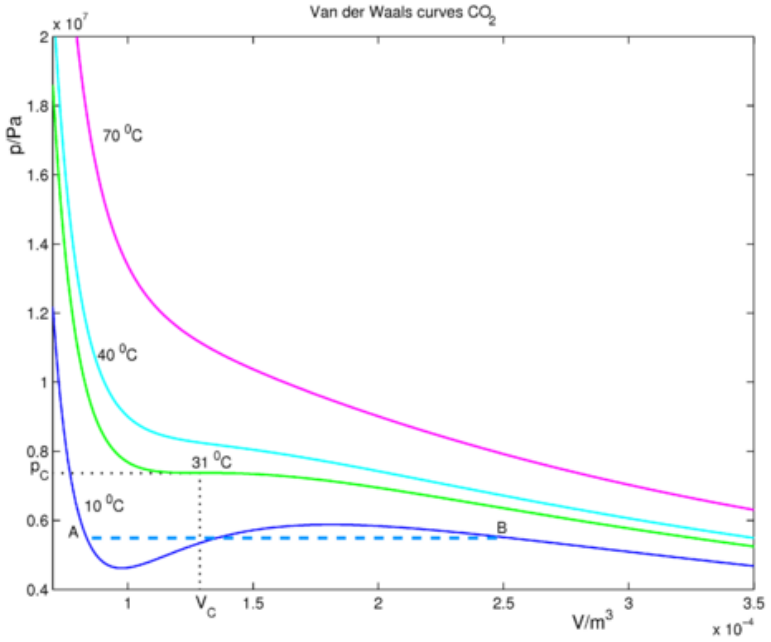


van der Waals ..equation

van der Waals …equation

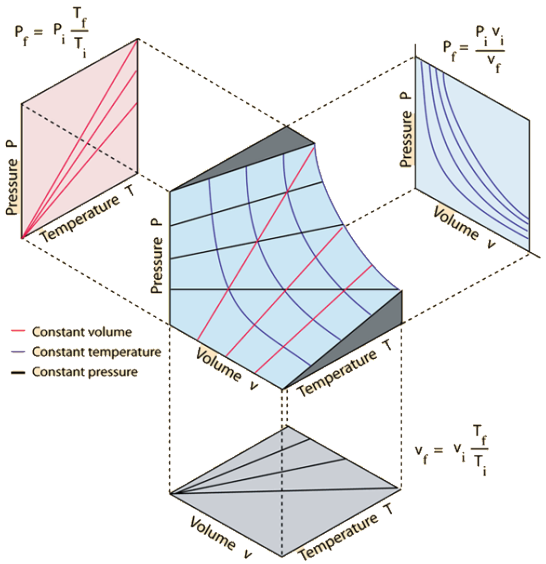
$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Repulsion Attraction



Critical temperature, T_C

Ideal

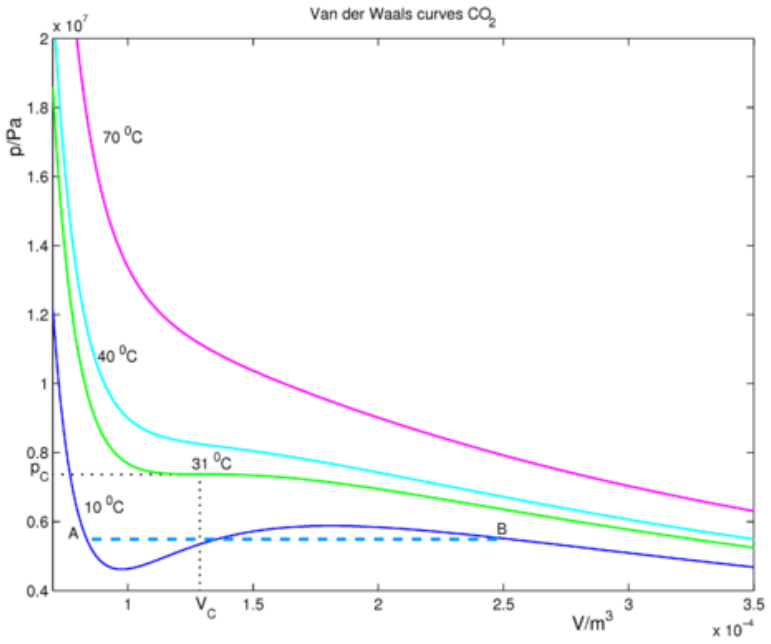


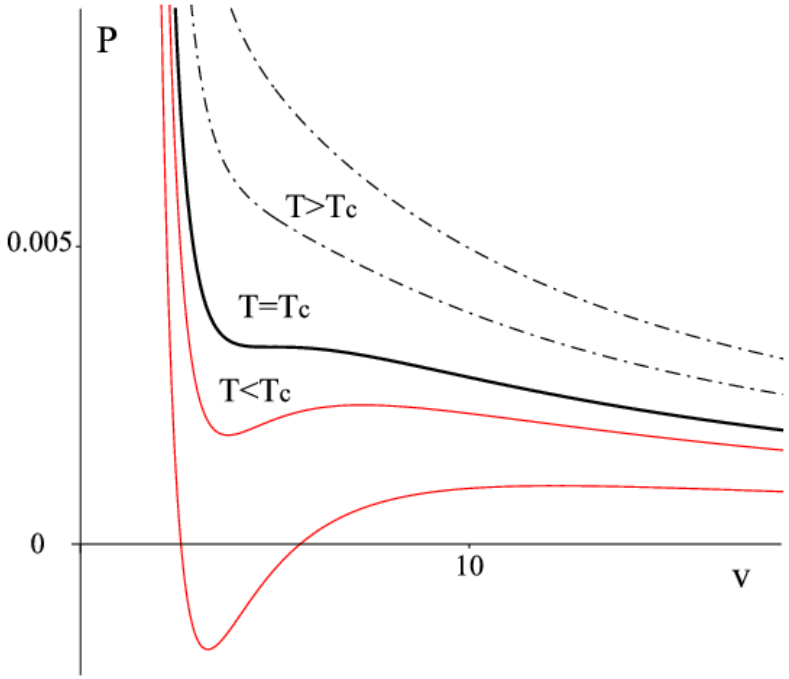
van der Waals ..equation

van der Waals …equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Repulsion Attraction





Critical temperature, T_c

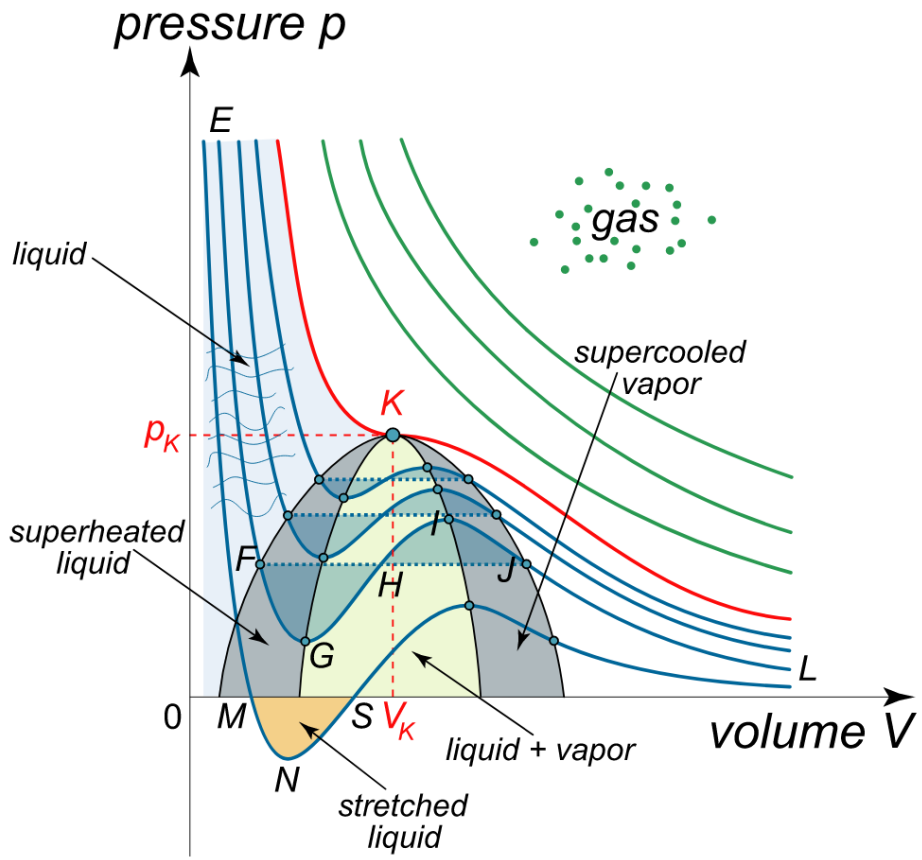
van der Waals ..equation

van der Waal …equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Repulsion

Attraction



van der Waals ..equation

The van der Waals equation is

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

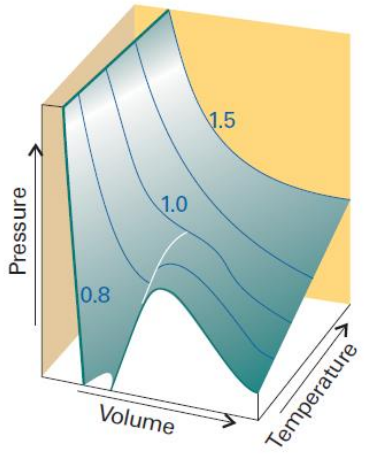
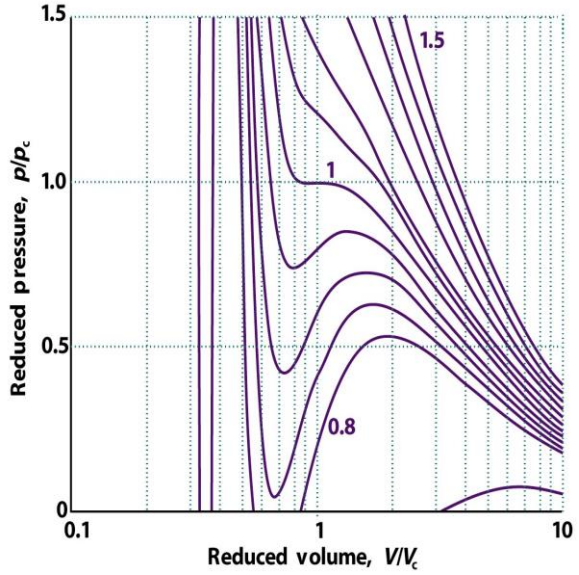


Fig. 1.17 The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.



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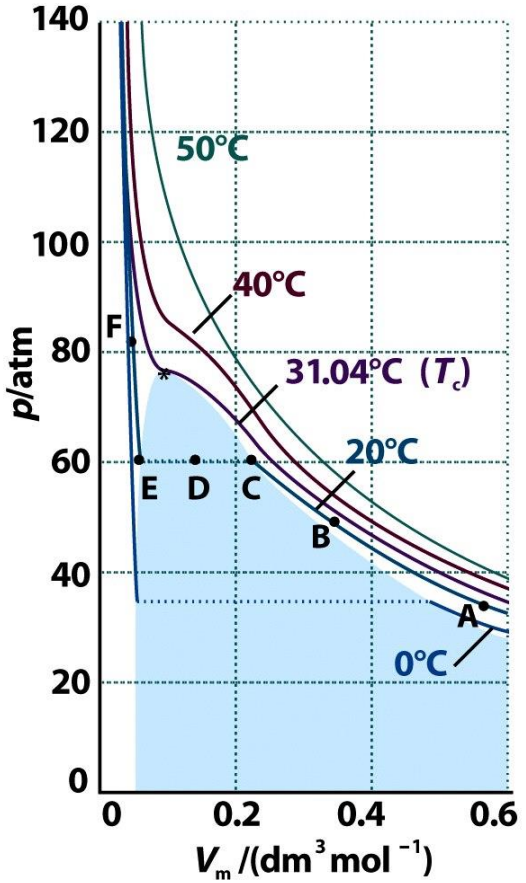

Figure 1-15
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