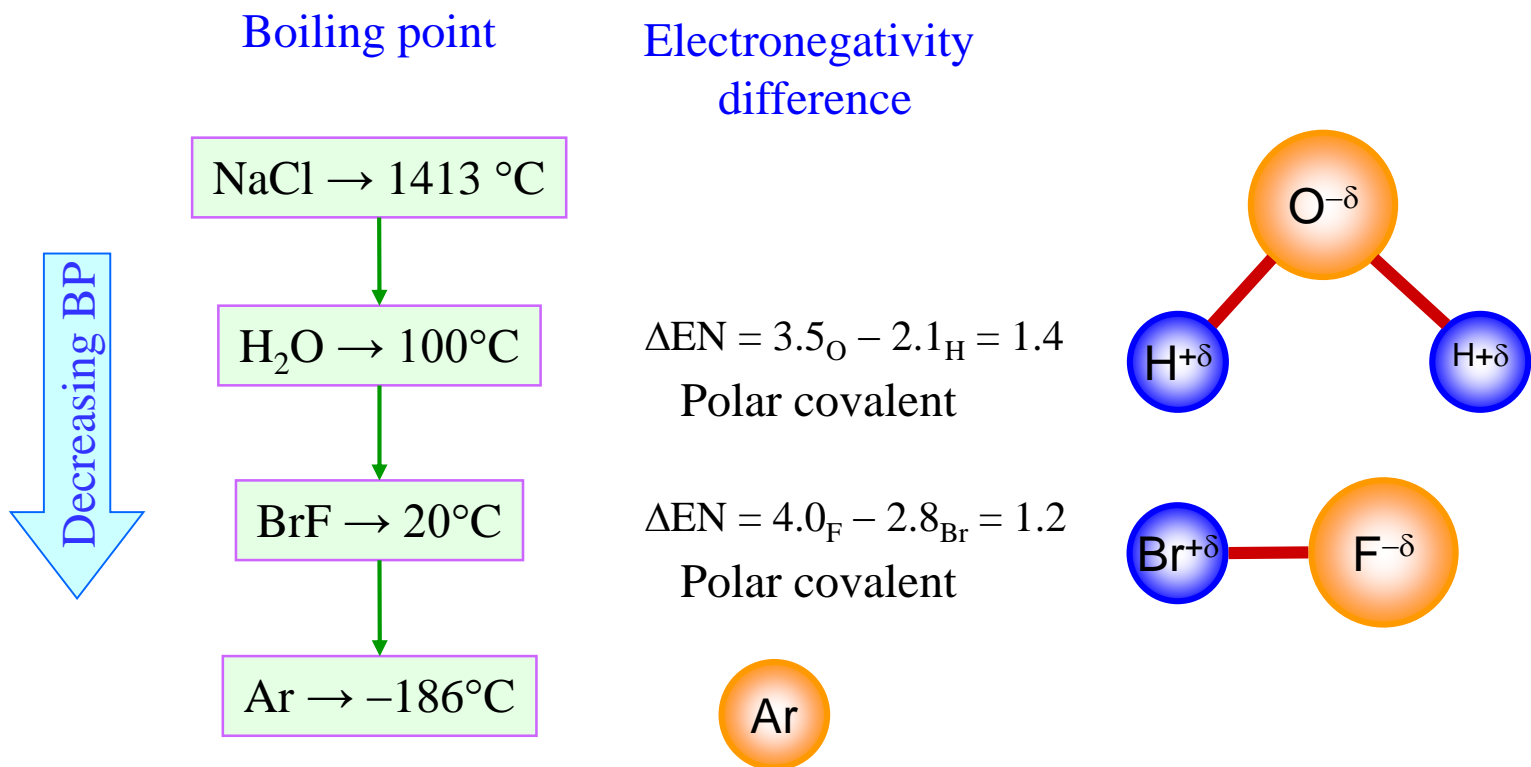


# Intermolecular forces

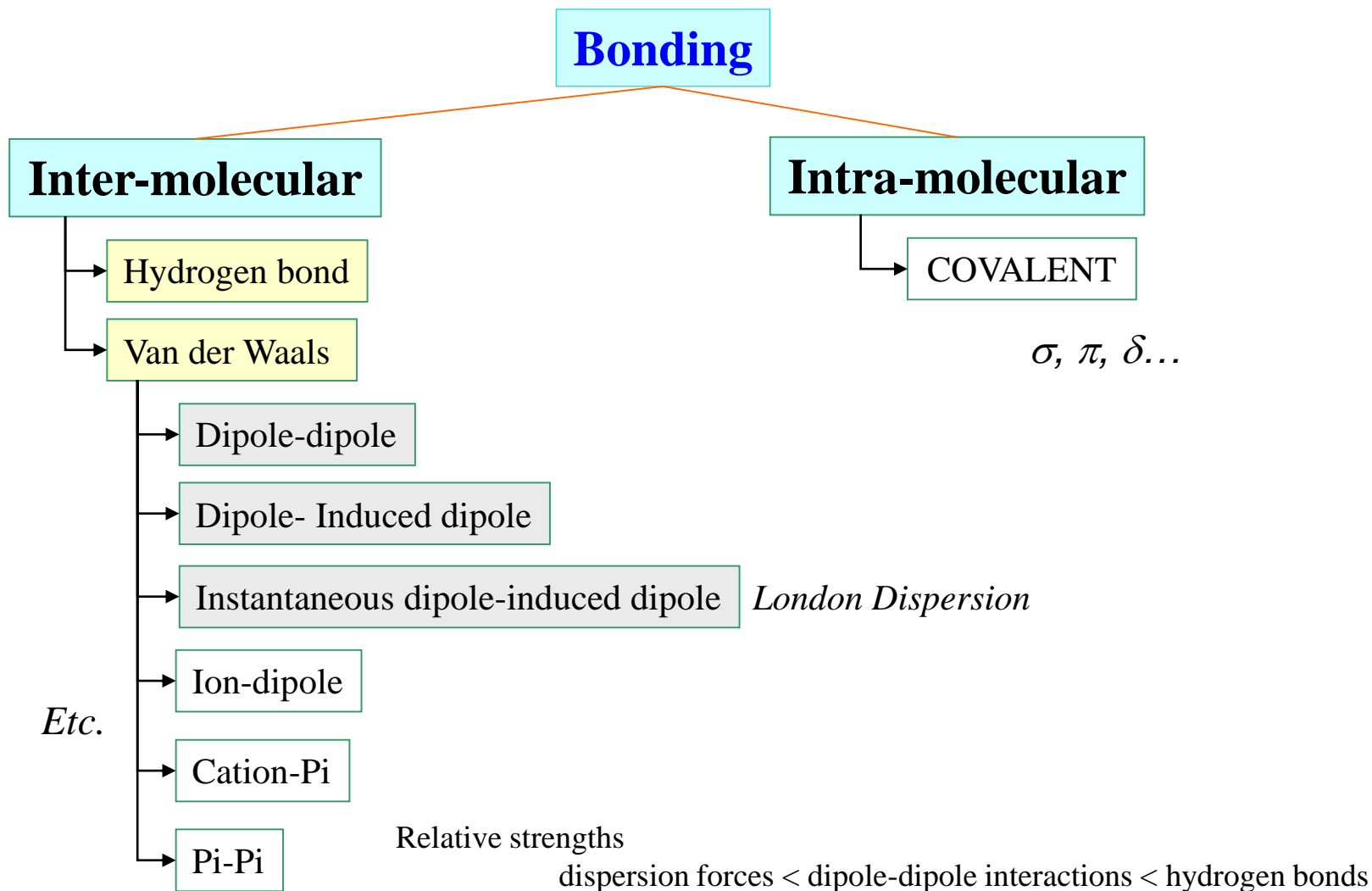
- ❑ Intermolecular weak interactions
- ❑ The strong 'bonds' are: Covalent, Ionic and Metallic

How do we get a measure of non-covalent interactions?

- ❑ **Boiling point** (being the temperature at which vapor pressure of substance equals the ambient pressure) is a better measure of non-covalent forces as compared to Melting point (which not only influenced by Attractive forces but also the crystal packing)

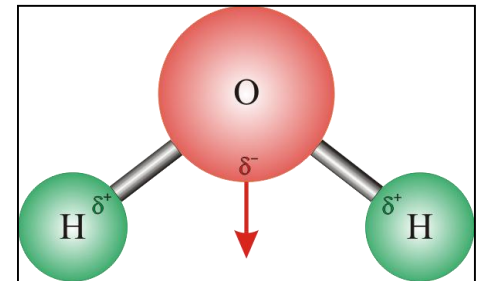
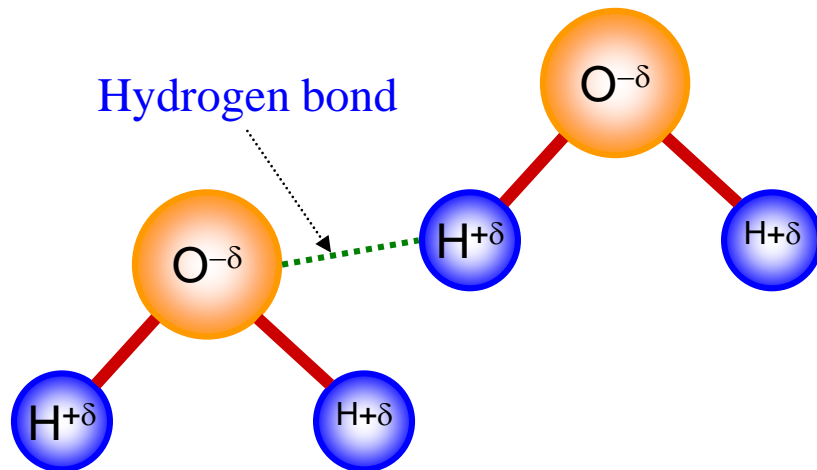


# Intermolecular forces



# Intermolecular forces - Hydrogen bond

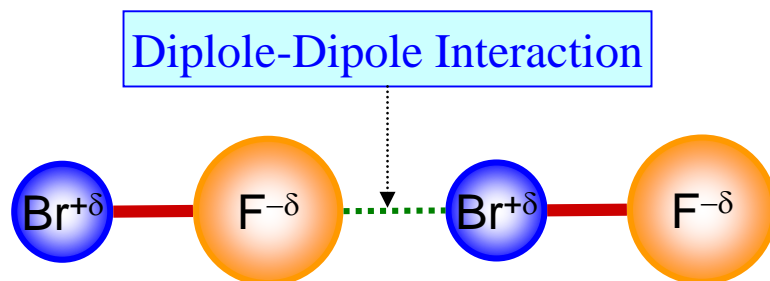
- The covalent bonding between a hydrogen atom and a strongly electronegative atom becomes 'polar'-covalent
- The 'charged' hydrogen 'ion' can be attracted to a electronegative atom, such as nitrogen, oxygen or fluorine
- hydrogen bond should not be confused with a covalent bond to hydrogen.
- Types of hydrogen bonds:
  - Intermolecular (between molecular)
  - Intramolecular (within a molecule)
- E.g. of hydrogen bonding: water (responsible for the high boiling point of water compared to say  $\text{H}_2\text{S}$ ), DNA, partly responsible for the secondary, tertiary, and quaternary structures of proteins and nucleic acids, Polymers



# Intermolecular forces – Van der Waals

## Dipole- Dipole interactions

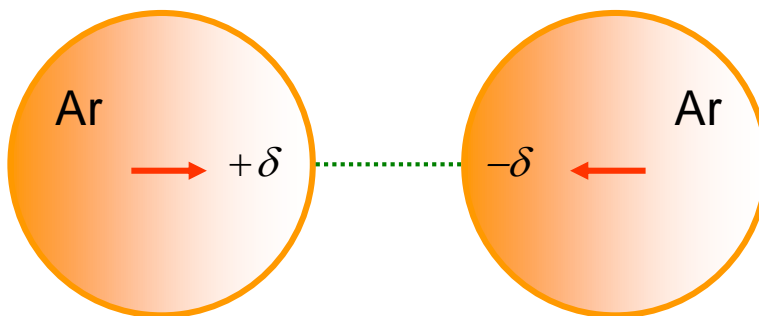
- In the covalent bonding between two atoms of very different electronegativity the bond becomes highly polar (introducing partial charges on the species)
- This dipole can interact with other permanent dipoles
- This interaction is stronger than dispersion forces



# Intermolecular forces – Van der Waals

## Instantaneous dipole-induced dipole (*London Dispersion*)

- Instantaneously generated dipole (due to asymmetry in electron charge distribution around the nucleus) on one atom leads to slight polarization of the atom
  - This induces a dipole on the neighbouring atom (temporarily)
- The force between these two dipoles is called the London dispersion forces
- The force is very weak and is temporally varying
- Can operate between non-polar molecules ( $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}_2$  etc.)
- The strength of the dispersion forces will increase with number of electrons in the molecule

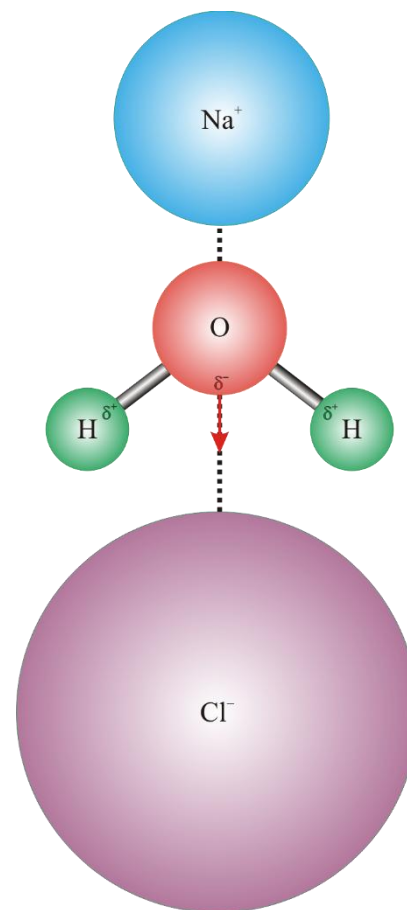


# Intermolecular forces – Van der Waals

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## Ion-Dipole

- Permanent dipole interacts with an ion.
- This explains for example the solubility of NaCl in water.
- The figure below shows the interaction of  $\text{Na}^+$  and  $\text{Cl}^-$  ions interacting with the permanent dipoles in a water molecule.



# Equation of State

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Early experiments on the variables of state (such as T, P, V, and n) showed that only two of these variables of state need to be known to know the state of a sample of matter.

An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when you want to know the effect of a change in one of the variables of state

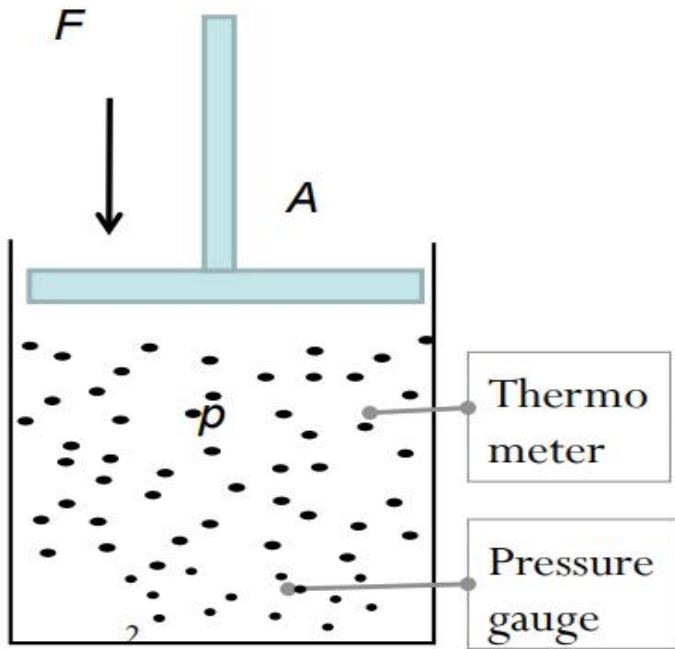
- **Solids and Liquids:** If the pressure on a solid or liquid is increased, the volume does not change much. If the temperature is increased, the volume doesn't change much either. Therefore, an appropriate equation of state describing such systems would be:

$$V(T, P) = \text{constant}$$

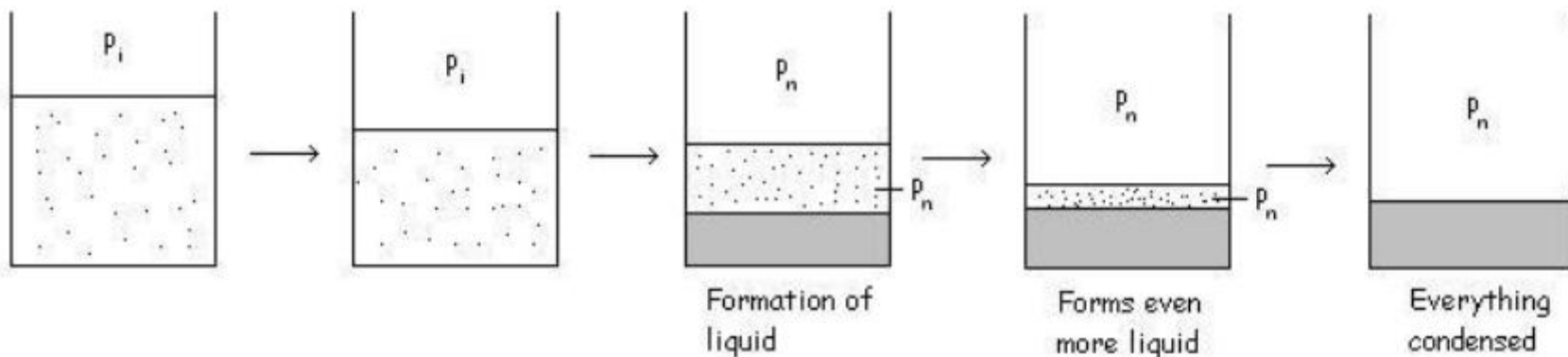
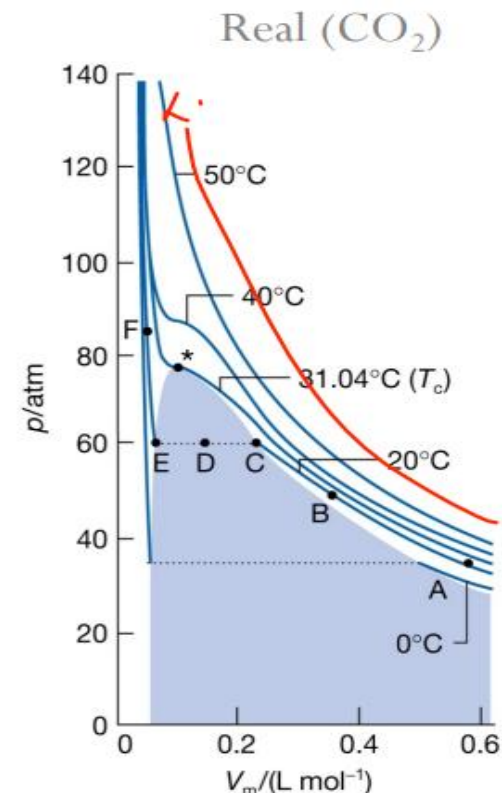
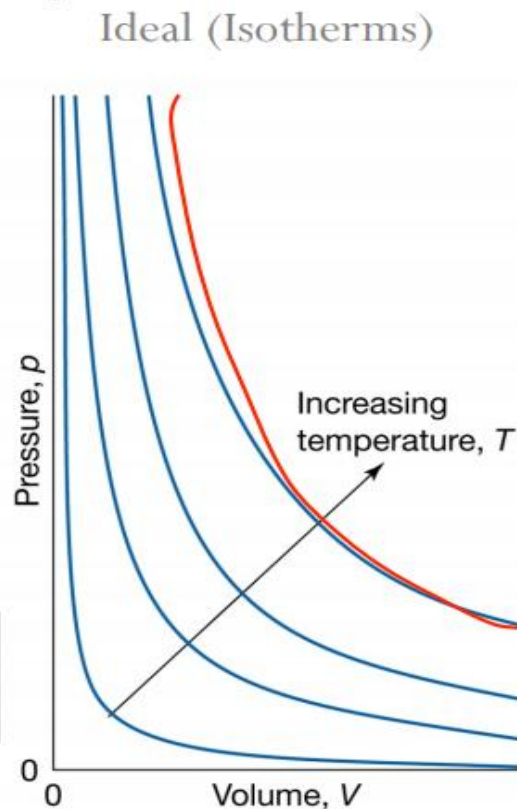
- **Gases:** In contrast, changing the pressure or temperature of a gas will have an easily observable effect on the volume of that gas. For an **ideal gas** (no intermolecular interactions and no molecular volume) an appropriate equation of state would be:

$$V(T, P, n) = (nRT)/P$$

# Equation of State



Chemical Thermodynamics : Georg Duesberg





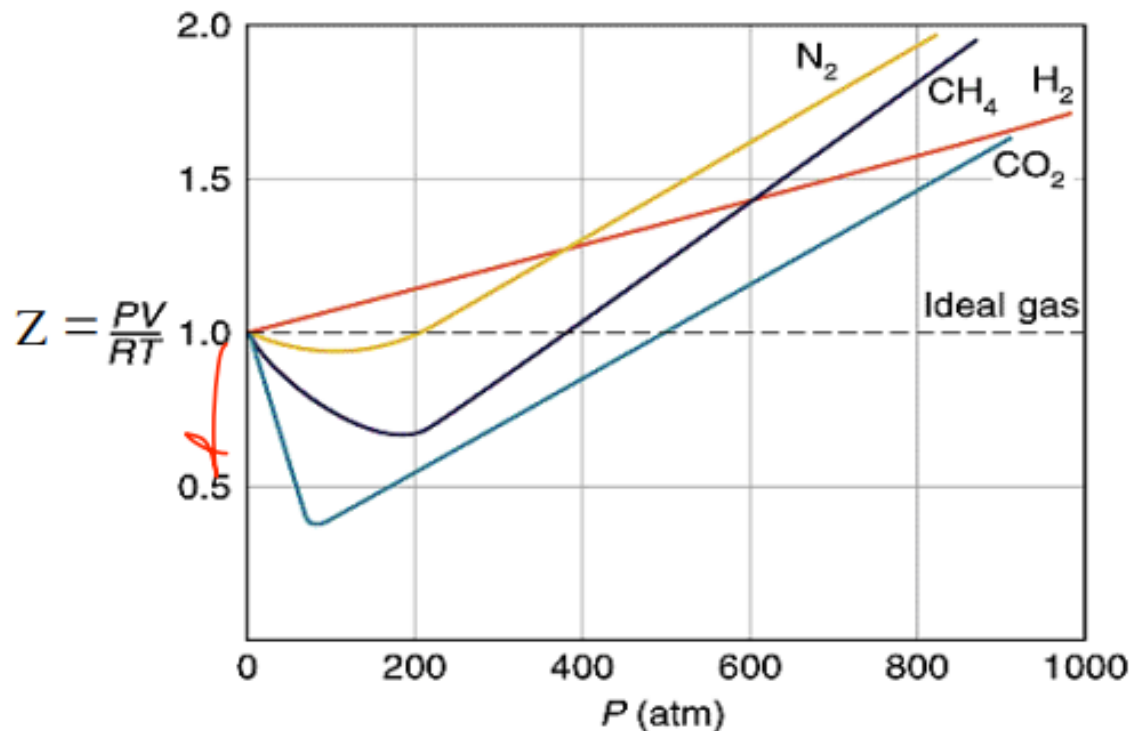
# Equation of State

## Deviations from Ideal Gas Behaviour: Nature of Gas

Deviations from ideality can be described by the COMPRESSION FACTOR,  $Z$  (sometimes called the compressibility).

$$Z = pV/(nRT) = pV_m/(RT) \quad \text{For ideal gases } Z = 1$$

- Attractive forces vary with nature of gas
- At High Pressures repelling forces dominate



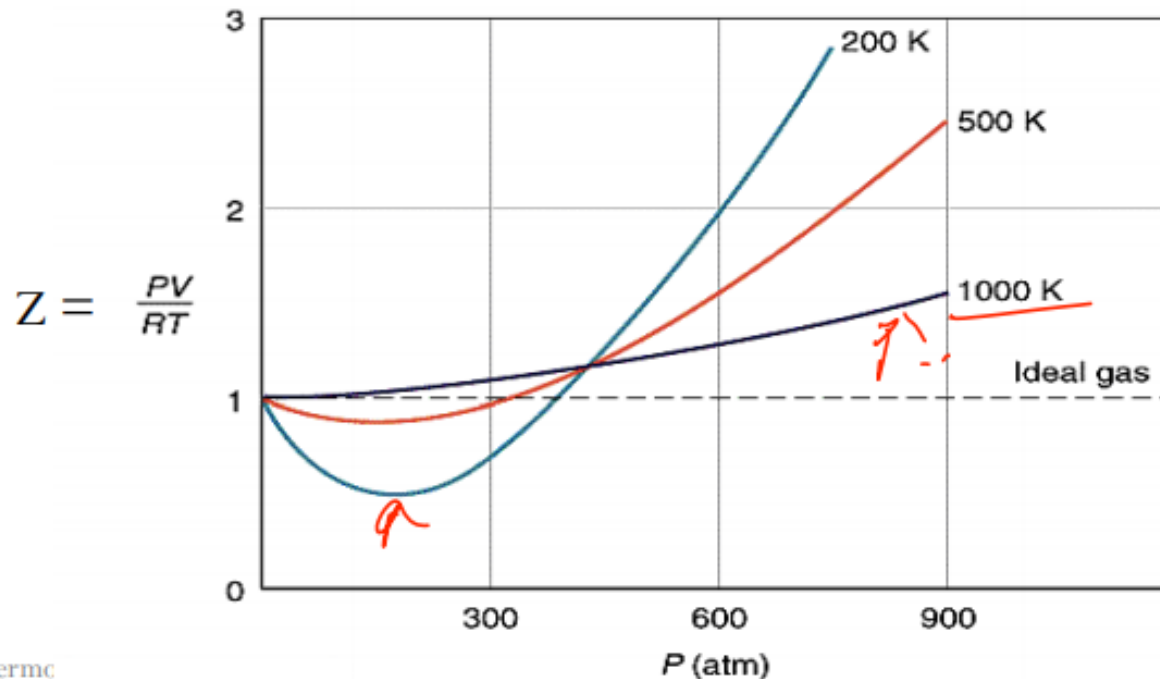
# Equation of State

## Deviations from Ideal Gas Behaviour: Temperature

Deviations from ideality can be described by the **COMPRESSION FACTOR**,  $Z$  (sometimes called the compressibility).

$$Z = pV/(nRT) = pV_m/(RT) \quad \text{For ideal gases } Z = 1$$

- At Low Temperatures the attractive regime is pronounced
- higher Temperature  $\rightarrow$  faster motion  $\rightarrow$  less interaction

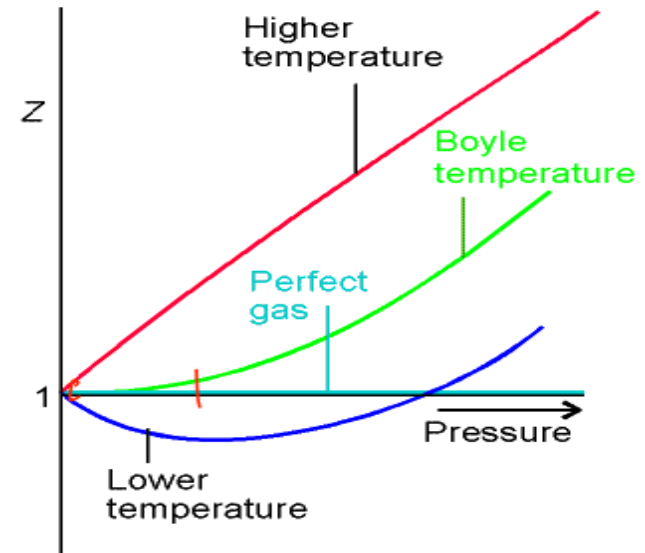


# Equation of State

**DEF** Compression diagram:  $Z - p$  curve

**please note:**

- at (almost) zero pressure  $Z = 1$
- for an ideal gas  $Z = 1$  always
- real gas, high pressure: high  $Z$
- at the Boyle temperature:  $Z$  starts horizontally
- below the Boyle temperature:  $Z$  starts below 1
- above the Boyle temperature:  $Z$  is always above 1



**DEF:** Boyle temperature:  $Z(p)$  starts horizontally at this temperature

**significance:** at the Boyle temperature the real gases behave (almost) like the ideal gases if the pressure is not very high (e.g.  $p < 30$  bar)

Boyle temperature for  $N_2$  : 54,05 °C (→ air behaves like an ideal gas at 298K)

shape of the  $Z(p)$  curve:

curvature downwards: attracting forces between the molecules

going up: repelling forces / own volume of the molecules

# Real Gas – Virial equation

---

There are many equations of state describing real gases. These equations take in consideration molecular volume and interactions.

## Virial Equation of State

$$PV_m = RT \left[ 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots \right]$$

This is the **virial equation of state** and B and C are the second and third **virial coefficients**.

The first is 1.

B and C are themselves functions of temperature, B(T) and C(T).

Usually  $B/V_m \gg C/V_m^2$

B = 0 at Boyle temperature

# Real Gas – Van der Waals equation

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

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

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

## Real gas – Van der Waals equation: a

2) There are attractive forces between real molecules, which reduce the pressure:  $p \propto$  wall collision frequency *and*  
 $p \propto$  change in momentum at each collision.

Both factors are proportional to concentration,  $n/V$ , and  $p$  is reduced by an amount  $a(n/V)^2$ , where  $a$  depends on the type of gas.

[Note:  $a/V^2$  is called the internal pressure of the gas].

Real gas molecules do attract one another ( $P_{id} = P_{obs} + \text{constant}$ )

$P_{id} = P_{obs} + a (n / V)^2$   $a$  is also different for different gases

$$\frac{n^2}{V^2} a$$

**$a$  describes attractive force between pairs of molecules. Goes as square of the concentration  $(n/V)^2$ .**

# Real Gas – Van der Waals equation

---

## Real gas – Van der Waals equation: b

1. The molecules occupy a significant fraction of the volume.
  - > Collisions are more frequent.
  - > There is less volume available for molecular motion.

Real gas molecules are not point masses

$$(V_{\text{id}} = V_{\text{obs}} - \text{const.}) \text{ or } V_{\text{id}} = V_{\text{obs}} - nb$$

– b is a constant for different gases

*Very roughly,  $b \sim 4/3 \pi r^3$  where r is the molecular radius.*

Other explanation:

What happens if we reduce  $T$  to zero. Is volume of the gas,  $V$ , going to become zero? We can set  $P \neq 0$ . By the ideal gas law we would have  $V = 0$ , which cannot be true. We can correct for it by a term equal to the total volume of the gas molecules, when totally compressed (condensed)  $nb$ . Now at  $T = 0$  and  $P \neq 0$  we have  $V = nb$ .

$$P(V - nb) = nRT$$

# Equation of State

---

There are **many other equations of state** for real gases

1) The Berthelot Equation.

Replace Van der Waals' "a" with a temperature dependent term,  $a/T$ :

$$[p + a/(V_m^2 T)] [V_m - b] = RT$$

2) The Dieterici Equation :  $[p \exp(a/V_m RT)] [V_m - b] = RT$

3) Redlich-Kwong

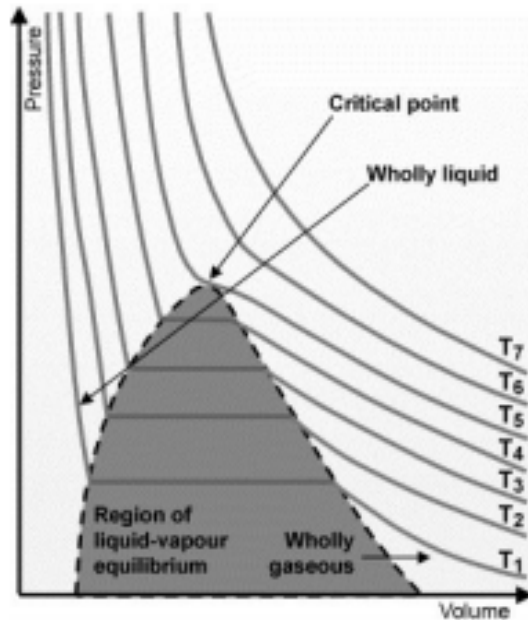
$$p = \frac{RT}{V_m - B} - \frac{A}{T^{1/2} V_m (V_m + B)}$$

4) Peng-Robinson

$$p = \frac{RT}{V_m - \beta} - \frac{\alpha}{V_m (V_m + \beta) + \beta (V_m - \beta)}$$



# Equation of State



measured isotherms of  $\text{CO}_2$

critical temperature: 304.3 K (31,1 °C)

critical pressure: 7.38 MPa (73,8 bar)

above the critical temperature:

gas

below the critical temperature:

vapour (liquefaction via compression)

grey area: vapour and liquid are in equilibrium at the vapour pressure

left of the gray area and below critical temperature:

liquid



# Equation of State - Critical

At the critical point:

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

Differentiating the van der Waals equation

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

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$$

Application of the conditions (2) gives

$$\frac{RT_c}{(V_{m,c} - b)^2} = \frac{2a}{V_{m,c}^3} \quad \text{and} \quad \frac{RT_c}{(V_{m,c} - b)^3} = \frac{3a}{V_{m,c}^4} \quad (3)$$

# Equation of State - Critical

From van der Waals equation:

$$P_c = \frac{RT_c}{V_{m,c} - b} - \frac{a}{V_{m,c}^2} \quad (4)$$

Division of the first equation in (3) by the second yields

$$\frac{\frac{RT_c}{(V_{m,c} - b)^2}}{\frac{RT_c}{(V_{m,c} - b)^3}} = \frac{\frac{2a}{V_{m,c}^3}}{\frac{3a}{V_{m,c}^4}} \Rightarrow V_{m,c} - b = \frac{2V_{m,c}}{3} \Rightarrow \boxed{V_{m,c} = 3b} \quad (5)$$

Use of (5) in the first equation in (3) gives

$$\frac{RT_c}{4b^2} = \frac{2a}{27b^3} \quad \text{and} \quad \boxed{T_c = \frac{8a}{27Rb}} \quad (6)$$

$$P_c = \frac{8a/27b}{2b} - \frac{a}{9b^2} = \frac{a}{27b^2} \quad \boxed{P_c = \frac{a}{27b^2}}$$

# Equation of State - Critical

---

Three equations for two parameters,  $a$  and  $b$

$$b = \frac{RT_c}{8P_c}$$

$$a = \frac{27R^2T_c^2}{64P_c}$$

Predicts the compressibility factor at the critical point

$$Z_c \equiv \frac{P_c V_{m,c}}{RT_c} = \frac{3}{8} = 0.375$$

$$\frac{P_c V_{m,c}}{RT_c} = 1 \quad \text{ideal gas}$$

## Equation of State

---

For nitrogen  $a=0.14$  and  $b=3.87 \times 10^{-5}$ . If 1.0 mole of nitrogen is confined to 2.00l and is at  $P=10\text{atm}$  what is  $T_{\text{ideal}}$  and  $T_{\text{vdW}}$ ?

$$PV = nRT \quad PV / nR = T \quad 10 \times 2 / 1 \times 0.082 = 244$$

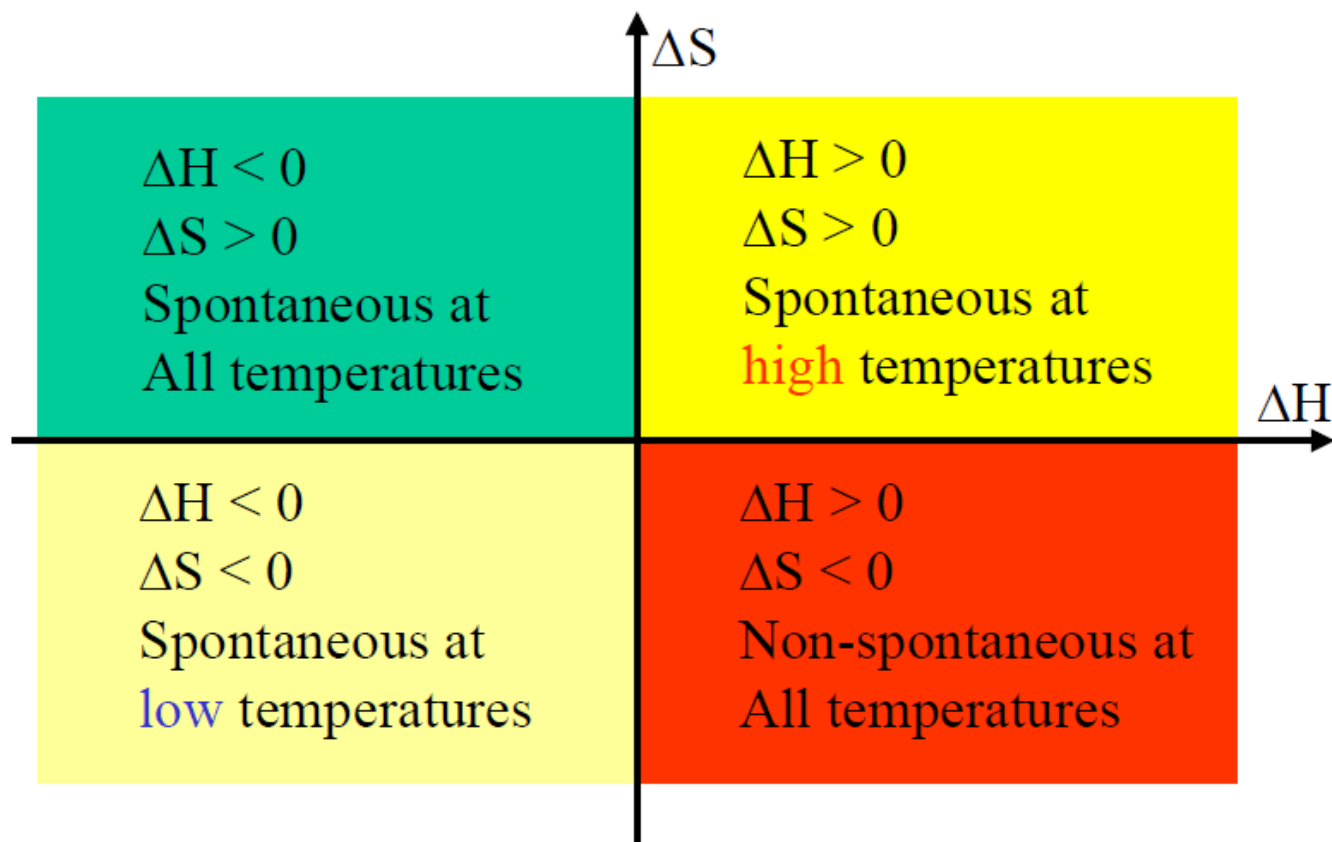
$$\left( P + a \left( \frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

$$\left( P + a \left( \frac{n}{V} \right)^2 \right) (V - nb) / nR = T$$

$$\left( 1 + 0.14 \left( \frac{1}{2} \right)^2 \right) (2 - 1 \times 0.0387) / 1 \times 0.082 = 240$$

# Estimations of Entropy and Free energy

$\Delta S_{\text{univ}}$	$\Delta G$ (P = const, T = const)	Process
$> 0$	$< 0$	Spontaneous
$< 0$	$> 0$	Nonspontaneous
$= 0$	$= 0$	Equilibrium



# Estimations of Entropy and Free energy

Predict which substance in each pair has the higher entropy. Assume there is one mole of each substance at 25 °C and 1 bar.

(a) Hg(l) or CO(g)

(b) CH<sub>3</sub>OH(l) or CH<sub>3</sub>CH<sub>2</sub>OH(l)

(c) KI(s) or CaS(s)

Calculate the entropy change when 2 moles of carbon monoxide condenses at its boiling point of -191.4°C. The heat of vaporization of CO is 6.04 kJ/mol.

$$n = 2 \text{ mol CO}$$

$$T_{\text{boil}} = (-191.4^{\circ}\text{C} + 273.15) = 81.75 \text{ K}$$

$$\Delta H_{\text{vaporization}} = 6.04 \text{ kJ/mol}$$

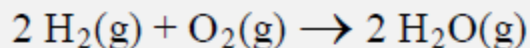
Use equation 19.2 to calculate  $\Delta S$  for this process. Remember that the gas condenses, the opposite of vaporization, so the sign of  $\Delta H_{\text{vaporization}}$  is reversed.

$$\Delta S_{\text{condense}} = -\Delta H_{\text{vaporization}}/T_{\text{boil}} = -(6.04 \text{ kJ/mol})(2 \text{ mol})/81.75 \text{ K} = -(0.1478 \text{ kJ/K})(1000 \text{ J/kJ}) = -148 \text{ J/K}$$

# Estimations of Entropy and Free energy

---

Hydrogen and oxygen react to form water vapor in a spontaneous reaction.



Predict the sign of the entropy change for this reaction and using Table 19.2

When hydrogen and oxygen gas react to form water vapor, 3 moles of gas are converted into 2 moles of gas, for every mole of reaction. The total number of moles of gas decreases, so  $\Delta S^\circ$  for this reaction should be negative.

Use standard molar entropy values and equation 19.3b to calculate the standard entropy change.

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= (2 \text{ mol})(S^\circ[\text{H}_2\text{O}(\text{g})]) - \{(2 \text{ mol})(S^\circ[\text{H}_2(\text{g})]) + (1 \text{ mol})(S^\circ[\text{O}_2(\text{g})])\} \\ &= (2 \text{ mol})(188.8 \text{ J/K}\cdot\text{mol}) - \{(2 \text{ mol})(130.7 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(205.1 \text{ J/K}\cdot\text{mol})\} \\ &= -88.9 \text{ J/K}\end{aligned}$$

The entropy change for this reaction is negative, as predicted based on the reaction stoichiometry.

# Estimations of Entropy and Free energy

Carbon monoxide and oxygen gas react to form carbon dioxide.



Calculate the standard free energy change for this reaction at 25<sup>0</sup>C from  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$ .

Step 1: Use standard heats of formation to calculate the enthalpy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ[\text{CO}_2\text{(g)}] - \Delta H_f^\circ[\text{CO(g)}] - \frac{1}{2} \Delta H_f^\circ[\text{O}_2\text{(g)}] \\ &= -393.5 \text{ kJ/mol} - (-110.5 \text{ kJ/mol}) - 0 \\ &= -283.0 \text{ kJ/mol}\end{aligned}$$

Step 2: Use standard entropy values to calculate the entropy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants}) \\ &= S^\circ[\text{CO}_2\text{(g)}] - \Delta S^\circ[\text{CO(g)}] - \frac{1}{2} S^\circ[\text{O}_2\text{(g)}] \\ &= 213.7 \text{ J/mol K} - (197.7 \text{ J/mol K}) - (\frac{1}{2})(205.1 \text{ J/mol K}) \\ &= -86.6 \text{ J/mol K}\end{aligned}$$

Note  $\Delta S^\circ_{\text{rxn}}$  is negative as predicted by the stoichiometry: 1.5 moles of gas goes to form 1 mole of gas.

Step 3: Calculate  $\Delta G^\circ_{\text{rxn}}$  using equation 19.9

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = -283.0 \text{ kJ/mol} - (298 \text{ K})(-86.6 \text{ J/mol K})(1 \text{ kJ}/1000 \text{ J}) = -257 \text{ kJ/mol}$$