

Thermodynamics: study of flow of heat

Began in 1800's, industrial revolution, fossil fuels, locomotives

Arrhenius first studied the effect of CO₂ on atmosphere – humans will be in trouble in 2000 years

Developed before atoms and molecules were known

Empirical rules and laws

Four Laws:

- 0th Law – defines temperature, T
- 1st Law – defines energy, U – conservation of energy
- 2nd Law – defines entropy, S – direction of time
- 3rd Law – Numerical value to the entropy

Systems

Surroundings

Boundary – between the system and the surrounding

Real or imaginary boundary

System:

- Open – allows mass and energy to freely flow through boundary
- Closed – energy flows, mass does not
- Isolated – neither flows

Describe the system

p, T, V, n_i, m

Homogenous or heterogeneous system

Equilibrium system – thermodynamics talks about these

Components

glass of water with ice – one component

coffee – milk, water, sugar... multicomponent

Extensive and Intensive properties

V, m – double as you double the system (extensive)

T, $\bar{V} = \frac{V}{n}$ - remain the same (intensive)

State variables – does not matter how the state has been achieved

One-component homogenous system

No. of moles, and two variables – enough to know the system

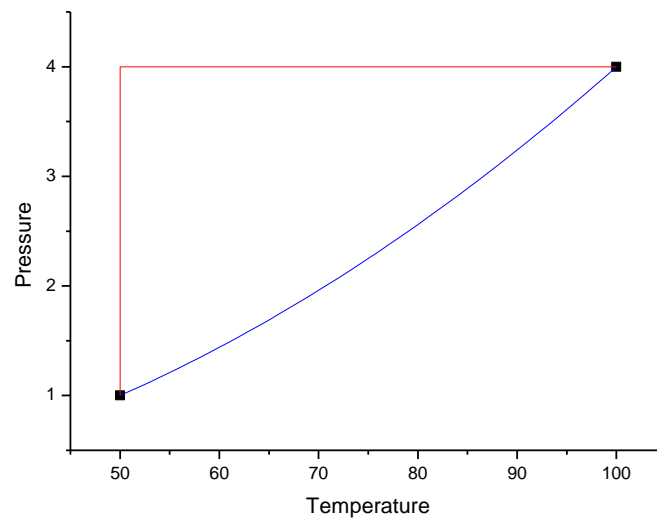
Chemical notation

$3 \text{ H}_2 (\text{g}, 1 \text{ bar}, 100 \text{ }^\circ\text{C})$

$5 \text{ H}_2\text{O} (\text{l}, 1 \text{ bar}, 25 \text{ }^\circ\text{C}) + 5 \text{ C}_2\text{H}_5\text{OH} (\text{l}, 1 \text{ bar}, 25 \text{ }^\circ\text{C})$

From one eq. state to another

$3 \text{ H}_2 (\text{g}, 4 \text{ bar}, 100 \text{ }^\circ\text{C}) \rightleftharpoons 3 \text{ H}_2 (\text{g}, 1 \text{ bar}, 50 \text{ }^\circ\text{C})$

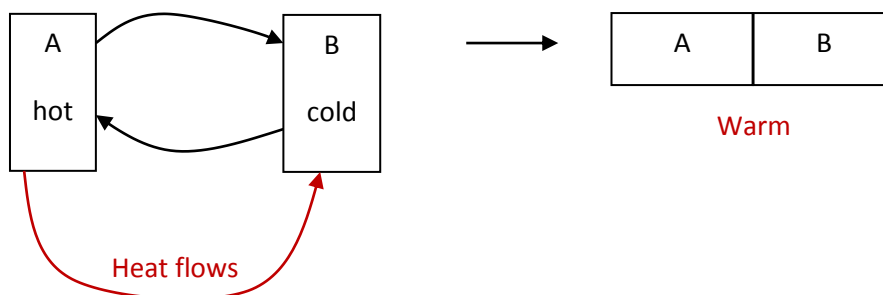


Path

- Reversible: slow
- Irreversible: sudden – gas molecules are agitated. All in different variables – also defines the direction of time

Some types of paths

- Adiabatic – no heat exchange
- Isobaric – constant pressure
- Isothermal – constant temperature

0th Law

If A and B are in thermal eq. and B and C are in thermal eq. then A and C will also be in thermal eq.

This allows us to define temperature – B could be a thermometer

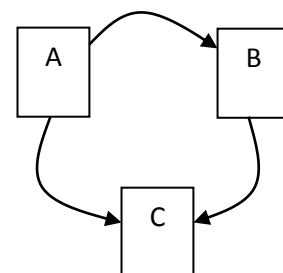
Concept of thermometer

Measurement of thermometer

Definition of scales: °C, K, °F

Requirements for a thermometer

- 1) Material – e.g. Hg
- 2) Property $f(t)$ – e.g. Volume
- 3) Reference points – e.g. mp, bp
- 4) Interpolation scheme



Temperature Scale

2 points of reference and then interpolation

Centigrade/Celcius: Vol. of Hg, freezing and boiling point of water

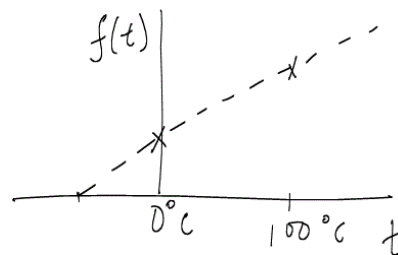
Romer (Denmark): 7.5 Romer freezing of water, 22.5 Romer temperature of warm blood

Fahrenheit (German): multiplied the Romer scale by 4 and then by 16/15 – m.p. 32 °F, b.p. 212, under armpit for a healthy human 96 (actually it is 98.6)

Ideal Gas Thermometer

$$f(t) = \lim_{p \rightarrow 0} p\bar{V}$$

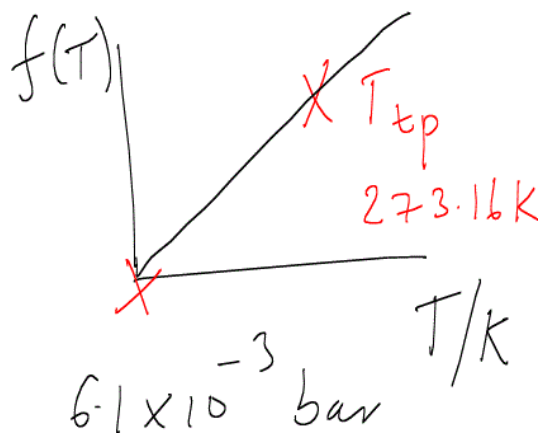
Absolute zero = 0 K = -273.15 °C



So lets change the zero to 0 K.

Linear in T $\therefore \lim_{p \rightarrow 0} p\bar{V} = f(T) = RT$ (pV is constant at a given T \rightarrow Boyle's Law)

or $p\bar{V} = RT$ **Ideal Gas**



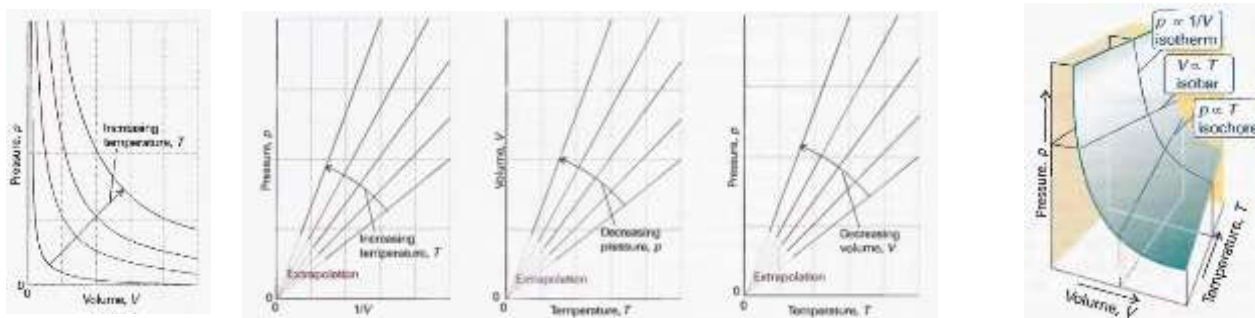
Boyle's Law: $pV = \text{constant}$, at given n, T

Charle's Law: $V = \text{const} \times T$, at given n, p

$P = \text{const} \times T$, at given n, V

Boyle's and Charle's Laws are limiting cases as $p \rightarrow 0$.

Avogadro's principle: $V = \text{const} \times n$ at given p, T (Equal volumes of gases at the same p and T contain the same numbers of molecules)



Dalton's Law:

Partial pressure of a gas in a mixture (ideal, real) $p_j = x_j p_{tot}$. When all gases are ideal – “The pressure exerted by a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone”

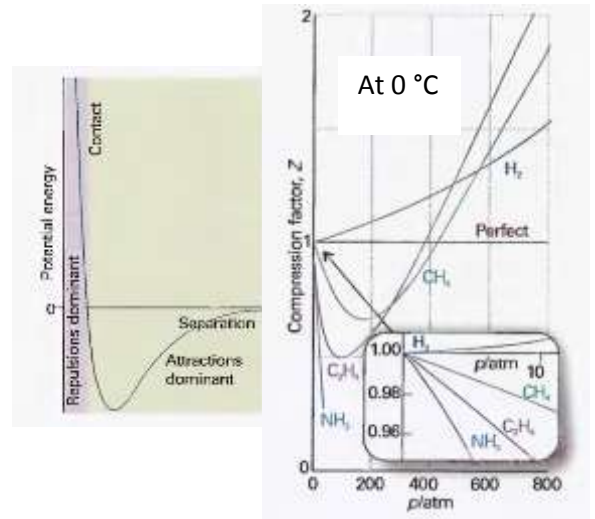
Compression factor Z

$$\frac{p\bar{V}}{RT} = Z \text{ or } Z = \bar{V}/\bar{V}_{IG} \text{ i.e. molar volume if gas were ideal}$$

Low p, $Z \approx 1$ molecules are far apart and there are no intermolecular forces

High p, $Z > 1$ indicating repulsion between molecules, therefore V is larger

Intermediate p, $Z < 1$ implies attractive forces are dominant



Virial Expansion

$$p\bar{V} = RT(1 + B'p + C'p^2 + \dots)$$

At low pressures, large molar volumes or high temperature, this reduces to the I.G. EOS

Alternately, in terms of molar volume,

$$pV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right)$$

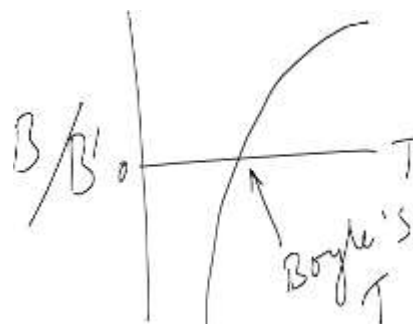
Usually, the 2nd coefficient is important

When B is ignored, I.G. EOS is obtained. However, many properties depend on the 1st derivative

$$\text{e.g. } \frac{dZ}{dp} = B' + 2pC' + \dots \rightarrow B' \text{ as } p \rightarrow 0 \text{ (For I.G. this would approach 0)}$$

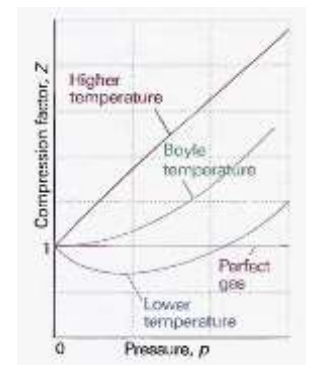
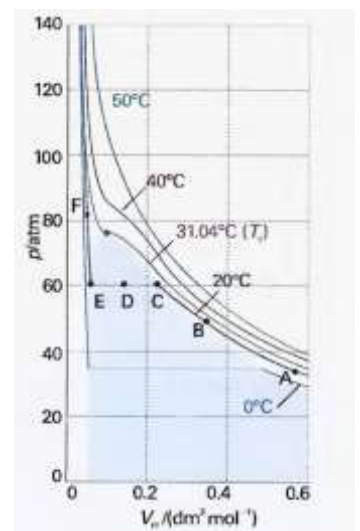
Coefficients are temperature dependent

Some temperature at which $B \rightarrow 0$, then $Z \rightarrow 1$. This is the Boyle's temperature, which of course is at low p, high V.



Condensation occurs moving on the line ABC by pushing a piston. At C, the gas is in equilibrium with the liquid and the piston slips towards CDE without any change in pressure. This pressure is called the vapour pressure of the liquid at that Temperature.

If compression is carried out at critical temperature, the two phases are not formed. $T > T_c$ supercritical fluid.

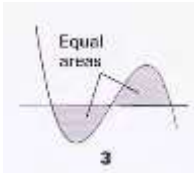


Van der Waals equation

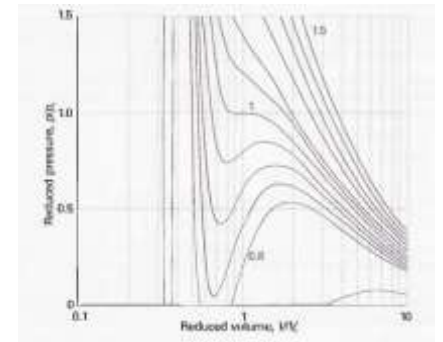
To account for the volume of the gas molecules, $p(V_m - b) = RT$

To account for the attractions between the gas molecules, $p(V_m - b) = RT - a/V_m^2$

The vdW EOS describes the isotherms as in the figure. Below T_c some loops appear because of the cubic nature of the equation. A method described as Maxwell construction is used to correct this.



- 1) IG isotherms at high T, large V_m
 - 2) Liquids and gases coexist when attraction and repulsions cancel (loops form when the two terms cancel)
 - 3) Critical constants are related to vdW's coefficients
- Critical point is an inflexion point. Hence, first and second derivatives should both be zero.



$$\frac{dp}{dV_m} = \frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

Which gives, $V_c = 3b$, $p_c = \frac{a}{27b^2}$, $T_c = \frac{8a}{27Rb}$ and $Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8}$ for all gases

Principle of Corresponding States

Reduced variables \rightarrow divide by the critical value. e.g. $p_r = p/p_c$

Real gases at same T_r and V_r exert the same $p_r \rightarrow$ principle of corresponding states

Express vdW eqn in terms of reduced variables $p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$

Then introduce the vdW coefficients in place of the critical constants $\frac{ap_r}{27b^2} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2V_r^2}$

On rearranging, $p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$ which does not depend on the nature of the gas!!!

The labels are T_r 's

