

Dalton's Law of partial pressures: states that the pressure exerted by a mix of ideal gases is the sum of the partial pressures each would exert if they were alone in the same volume:

$$p_{\text{total}} = p_1 + p_2 + \dots + p_n \quad \text{or} \quad p_{\text{total}} = \sum_{i=1}^n p_i$$

The partial pressure, p_i , of one of the gases can be calculated by multiplying the gas mole fraction, x_i , by the total pressure of all the gases, p_{total} .

Perfect Gas Law: $pV = nRT$, R = ideal gas constant.

Combined Gas Laws: $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$.

Virial equation of state: This improves the perfect gas law because it takes into account intermolecular forces.

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

$V_m = \frac{V}{n}$ = molar volume, B, C etc are the **virial coefficients**. Observe that when the molar volume is very large, the terms $\frac{B}{V_m}$ and $\frac{C}{V_m^2}$ become increasingly less important, and in the limit we obtain the ideal gas law.

Van der Waals equation takes into account the finite distance between molecules and interparticle attractions:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{or} \quad \left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

a is a measure of attraction between particles, b is the volume excluded by a mole of particles.

Phases

Gibbs' phase rule: $F = C - P + 2$, where F is the number of degrees of freedom, C = number of independent components, P = the number of phases in equilibrium with each other. This is a relationship used to determine the number of state variables, F , chosen from amongst temperature, pressure and species compositions in each phase, which must be specified to fix the thermodynamic state of a system in equilibrium.

Clapeyron equation relates change in pressure to change in temperature at a phase boundary. The slope of the phase boundary is $\frac{dp}{dT}$.

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

Here ΔH = molar enthalpy of transition, ΔV = change in molar volume during transition.

Clausius-Clapeyron equation is an approximation of the Clapeyron equation for a liquid-vapour phase boundary. Plotting vapour pressure for various temperatures produces a curve. For pure liquids, plotting $\ln \frac{p}{p^\ominus}$ against $\frac{1}{T}$ produces a straight line with gradient $-\frac{\Delta H}{R}$. (Here, p^\ominus = any standard pressure).

$$\ln \frac{p_1}{p_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Here ΔH = molar enthalpy of vaporisation. This equation relates the natural logarithm of the vapour pressure to the temperature at a phase boundary.