Equations – P-Chem

GASES

Gas laws

atm = 1.01325 bar = 101325 Pa   bar = 1.0×10^5 Pa   torr = mmHg = 133.322 Pa

atm = 760 torr

Ideal gas law	$pV = nRT = \frac{m}{M}RT$ (p Pa, V m^3, T K)	
	$pM = \rho RT$ (M mole wt, ρ g/dm^3)	
van der Waals law	$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{V_r^2}$
	$p = \frac{RT}{V_m-b} - \frac{a}{V_m^2}$ [V_m molar vol = $\frac{V}{n}$]	
Berthelot	$p = \frac{nRT}{V-nb} - \frac{an^2}{TV^2}$	$p_r = \frac{8T_r}{3V_r-1} - \frac{3}{T_rV_r^2}$
Dieterici	$p = \frac{RTe^{(\frac{-na}{RTV})}}{V-nb}$	$p_r = \frac{T_re^{2(1-\frac{1}{V_rT_t})}}{2V_r-1}$
Virial	$p = \frac{nRT}{V}\{1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2}\}$	

quant reduced form $X_r = X/X_c$

molar fraction $x_j = \frac{n_j}{n}$; $n_j = nx_j$

Kinetic model

Collision cross sectional area	$\sigma = \pi d^2$
	$<V_x^2> = <V^2>/3$
Mean square speed	$<\nu>^2 = \frac{3RT}{M} = \frac{3kT}{m}$
Root mean square	$\nu_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$
Mean speed	$<\nu> = \nu_{rms}(8/3\pi)^{1/2} = (8RT/M\pi)^{1/2}$
Most probable speed	$\nu_{mp} = \nu_{rms}(2/3)^{1/2} = \sqrt{\frac{2RT}{M}}$
Relative mean speed	$\nu_{rel} = <\nu>\sqrt{2} = \nu_{rms}\sqrt{\frac{16RT}{3\pi}} = \sqrt{\frac{16RT}{\pi M}}$ (identical molecules)
	$\mu = \frac{M_AM_B}{M_A+M_B}$
	$\nu_{rel} = \sqrt{\frac{8RT}{\pi\mu}}$ (non-identical molecules)
Mean translational energy	$<E_{trans}> = \frac{mv^2}{2} = \frac{3}{2}pV = \frac{3}{2}RT$
Collision Frequency	$z = \sigma\nu_{rel}\mathcal{N} = \frac{\sigma v_{rel}\,p}{kT}$ (particles) $= \frac{pN_A}{2\pi MRT}$ (walls/container)
Mean free path	$\lambda = \nu_{rel}/z = \frac{kT}{p\sigma}$ (other atoms static) $= \sqrt{2}\,\frac{kT}{p\sigma}$ (all atoms dynamic)
Compression factor	$Z = \frac{V_m}{V_m^0} = \frac{pV_m}{RT} = \frac{pV}{nRT}$
Boyle Temperature	$T_B = \frac{a}{bR} = \frac{27}{8}T_C$
Effusion rate	$\frac{rate_a}{rate_b} = \sqrt{\frac{M_b}{M_a}}$

Constants

R = Gas constant = $N_A k$ *(8.31446 J/Kmol or Pa m³ /K mol)* = 0.0831445 *(dm³ bar /K mol)*
= *(0.0820574 dm³ atm /K mol)* = *(62.364 dm³ Torr/K mol)* = *(1.98721 cal/K mol)*

k = Boltzmann's constant *(1.38065x10⁻²³ J/K)*

Legend

d = distance, Collision diam	A = area	σ = collision cross-sectional area
V = volume	V_m = molar volume (V/n)	V_m^0 = molar vol of ideal gas
ν = velocity/speed	ν_{rms} = root mean square velocity	$\langle\nu\rangle = \nu_{mean}$ = mean speed
ν_{mp} = most probable speed	ν_{rel} = relative mean speed	$\langle E_{trans}\rangle$=mean translational energy
z = collision frequency	λ = mean free path	
E = Energy; electric field (J; N/C or V/m)	J = Joules (Nm or kg m^2/s^2)	
M = molar mass (Kg/mol)	F = force (N; Kg m/s^2)	p = pressure (N/m^2)
N = total molecules	N_A = Avogadro's number	$\mathcal{N}$ = number density (N/V)
R = Gas constant = $N_A k$ *(8.31446* J/Kmol)	k = Boltzmann's constant *(1.38065x10⁻²³ J/K)*	
Z = compression factor (= $\frac{V_m}{V_m^0}$)		

Gas Critical Constants

Constants	p_C	V_C	T_C
van der Waals law	$\frac{a}{27b^2}$	3b	$\frac{8a}{27bR}$
Berthelot	$\frac{1}{12}\sqrt{\frac{2aR}{3b^3}}$	3b	$\frac{2}{3}\sqrt{\frac{2a}{3bR}}$
Dieterici	$\frac{a}{4e^2b^2}$	2b	$\frac{a}{4bR}$

Notes:

1 Perfect gas isotherms are obtained at high temps & high V_M
2 Liquids and gases coexist when attractive and repulsive forces balance
3 Critical constants (and Boyle temp) are related to the van der Waals constants
4 For T< T_c isotherms oscillate

$$Z_c = \frac{3}{8} = \frac{P_c V_c}{RT_c}$$

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

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

$$p_r\, p_c = \frac{RT_rT_c}{V_rV_c-b} - \frac{a}{V_r^2V_c^2}$$