# Equations – P-Chem

## Internal Energy/Enthalpy

### Internal Energy

A=C & B=C, then A=B — $0^{th}$ Law of Thermodynamics

$U_{univ} = U_{sys} + U_{surr}$ = constant — $1^{st}$ Law of Thermodynamics *(energy cannot be created/destroyed)*

$U_{perfect} = \frac{1}{2} m\langle v\rangle^2 = \frac{1}{2} m \frac{3kT}{m} = \frac{3}{2}kT$ — perfect (monoatomic) gas

$E_{univ} = E_{sys} + E_{suff}$ — ($E_{univ}$ = const)

$\Delta U_{sys} = q + w$ — (q or w in = positive, out = negative)

*[volume decreases=w+, $\Delta U_{sys}$ increases; q (heat) enters (+q), $\Delta U_{sys}$ increases]*

$H = U + pV = U + n_gRT$; — Enthalpy

$\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(n_gRT)$

$H = C\Delta T = q$

$$dU = \left(\frac{\delta U}{\delta T}\right)_V dT + \left(\frac{\delta U}{\delta V}\right)_T dV = C_V\, dT + \pi_T\, dV; \quad \left(\frac{\delta U}{\delta T}\right)_p = \alpha\pi_T V + C_V = \pi_T\left(\frac{\delta V}{\delta T}\right)_p + C_p$$

$$dP = \left(\frac{\delta p}{\delta T}\right)_V dT + \left(\frac{\delta p}{\delta V}\right)_T dV$$ Exact differential

$$dP = \frac{\alpha}{\kappa_T}\, dT - \frac{1}{\kappa_T V}\, dV$$ General

$$C_V = \left(\frac{\delta U}{\delta T}\right)_V \;;\; C_p = \left(\frac{\delta H}{\delta T}\right)_p \;;\; \left(\frac{\delta H}{\delta p}\right)_T = V(1-\alpha T)$$

$C_{V,s} = \frac{C_V}{m}$ ; $q = mC_{V,s}\Delta T$ — Specific Heat Capacity (heat needed to raise 1g of a sys 1° C ($\frac{J}{g\,K}$)

$C_{V,m} = \frac{C_V}{n}$ ; $q = nC_{V,m}\Delta T$ — Molar Heat Capacity (heat needed to raise 1mol of a sys 1° C ($\frac{J}{mol\,K}$)

### Perfect Gases

Internal Energy and Molar Heat capacity

| | *Monoatomic* | *Diatomic (2° freedom)* | *Polyatomic (linear)* |
|---|---|---|---|
| Internal Energy | $U = \frac{3}{2}nRT$ | $U = \frac{5}{2}nRT$ | $U = \frac{6}{2}nRT$ |
| Isochoric | $C_{V,m} = \frac{3}{2}R$ | $C_{V,m} = \frac{5}{2}R$ | $C_{V,m} = \frac{6}{2}R$ |
| Isobaric | $C_{P,m} = \frac{5}{2}R$ | $C_{P,m} = \frac{7}{2}R$ | $C_{P,m} = \frac{8}{2}R$ |

| Expansion | *Reversible* | *Irreversible* |
|---|---|---|
| Isothermal | $w = \int_{V_f}^{V_i} P_{gas}dV = nRT\ln(\frac{V_i}{V_f})$ | $w = -P_f\,\Delta V$ |
| Adiabatic | $T_f = T_i\,(\frac{P_f}{P_i})^{\frac{R}{C_p}} = T_i\,(\frac{V_i}{V_f})^{\frac{R}{C_{V,m}}}$ | $T_f = T_i\,(\frac{C_V}{C_p} + \frac{RP_f}{C_pP_i})$; $\Delta U = -p_f\Delta V = nC_V\Delta T$ |

| Intermediate constants | Isobaric | isothermal |
|---|---|---|
| gases | $\alpha = \frac{C_p}{C_v} = \frac{1}{V_i}(\frac{\delta V}{\delta T})_p$ | $\mathcal{K}_T = -\frac{1}{V}(\frac{\delta V}{\delta P})_T$ |
| solids/liquids (small ΔV) | $\alpha = \frac{1}{V_i}(\frac{V_f-V_i}{T_f-T_i})_p$ | $\mathcal{K}_T = -\frac{1}{V}(\frac{V_f-V_i}{p_f-p_i})_T$ |

$\mathcal{V}_{sound} = \sqrt{\alpha\frac{p}{\rho}}$ — Speed of sound in a gas

### Joule-Thompson effect

$\mu = \left(\frac{\delta T}{\delta p}\right)_H$ — Joule-Thompson coefficient

$dH = C_pdT - \mu C_pdp$

## Internal Pressure

$\pi_T = (\frac{\delta U}{\delta V})_T = T\,(\frac{\delta p}{\delta T})_V - p$

$\pi_T = 0$ for perfect gases and ~0 for liquids/solids

$\pi_T = \frac{an^2}{V^2} = \frac{a}{V_M^2}$ *for Van der Waal gases*

## Solids/liquids

$\Delta p = \frac{\alpha}{\kappa_T}\Delta T - \frac{1}{\kappa_T}\ln(\frac{V_f}{V_i})$

(small ΔV cont) $V_f = V_i\,(1 + \alpha(T_f - T_i))$ $V_f = V_i\,(1 - \kappa_T(p_f - p_i))$

## Adiabatic

$w_{adiab} = nC_{V,m}\Delta T = \Delta U$ perfect gas

$T_f = T_i\,(\frac{V_i}{V_f})^{\frac{R}{C_{V,m}}} = T_i\,(\frac{p_f}{p_i})^{\frac{R}{C_{p,m}}}$ perfect gas, reversible, adiabatic

$p_f = p_i(\frac{V_i}{V_f})^{\frac{C_{p,m}}{C_{V,m}}}$ perfect gas, reversible, adiabatic

$p_f T_i^c = p_i T_f^c$ perfect gas, reversible, adiabatic $c = \frac{C_{V,m}}{R}$

$p_i V_i^\gamma = p_f V_f^\gamma$ perfect gas, reversible, adiabatic $\gamma = \frac{C_{p,m}}{C_{V,m}}$

## Thermochemistry

$\Delta H^{\Theta}(T_2) = \Delta H^{\Theta}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\Theta}\, dT$ $\Delta_r C_p^{\Theta} = \sum_{\text{Prooducts}} \nu C_{p,m}^{\Theta} - \sum_{\text{Reactants}} \nu C_{p,m}^{\Theta}$

$\Delta_r U^{\Theta} = \Delta_r H^{\Theta} - (\Delta n_g)RT$ for Perfect Gases

**Important definitions for Perfect Gas**

Isothermal process, constant temp: $\Delta T = \Delta U = 0$; $q = -w$
Isochoric process, constant volume: $\Delta U = q$; $w = 0$
Isobaric process, constant pressure: $w = -p\Delta V$
Adiabatic process, no heat exchange: $\Delta U = w$; $q = 0$

## *Constants*

R = Gas constant = $N_A$k *(8.31446 J/Kmol or Pa $m^3$ /K mol)* = 0.0831445 *($dm^3$ bar /K mol)*
= *(0.0820574 $dm^3$ atm /K mol) = (62.364 $dm^3$ Torr/K mol) = (1.98721 cal/K mol)*
k = Boltzmann's constant *($1.38065\times10^{-23}$ J/K)*
$C_s$ water = 4.184 $(\frac{J}{g\,K}) = 1\,\frac{cal}{g\,K}$ ; $C_m$ water = 75.4 $(\frac{J}{mol\,K})$
atm = 1.01325 bar = 101325 Pa = 760 torr
bar = $1.0\times10^5$ Pa torr = mmHg = 133.322 Pa

## *Legend*

d = distance, Collision diam
V = volume
$\nu$ = velocity/speed
$\nu_{mp}$ = most probable speed
z = collision frequency
M = molar mass (Kg/mol)
N = total molecules
E = Energy; electric field (J; N/C or V/m)
U = internal energy (J)
$\pi_T$ = Internal pressure $(\frac{J}{m^3})$
$C_{V,s} = C_s$ = Specific Heat Capacity $(\frac{J}{<unit>\,K})$
R = Gas constant = $N_A$k *(8.31446* J/Kmol)

A = area
$V_m$ = molar volume (V/n)
$\nu_{rms}$ = root mean square velocity
$\nu_{rel}$ = relative mean speed
$\lambda$ = mean free path
F = force (N; Kg $m/s^2$)
$N_A$ = Avogadro's number
J = Joules (Nm or kg $m^2/s^2$)
w = work (J)
$\alpha$ = expansion coefficient
$C_{V,m} = C_m$ = Molar Heat Capacity,V
k = Boltzmann's constant *($1.38065\times10^{-23}$ J/K)*

$\sigma$ = collision cross-sectional area
$V_m^0$ = molar vol of ideal gas
$<\nu> = \nu_{mean}$ = mean speed
$<E_{trans}>$=mean translational energy
n = moles (mol)
p = pressure ($N/m^2$)
$\mathcal{N}$ = number density (N/V)
H = Enthalpy (J)
q = heat energy (J)
$\kappa_T$ =compressibility coefficient
$C_{V,m}$ = Molar Heat Cap, const p