

*Physical chemistry: a wealth of partial derivatives ... but they all mean something.*

$C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V$	Heat capacity at constant volume. (J/K; $C_{V,m}$ =J/mol·K). $C_V > 0$ .
$C_p \equiv \left( \frac{\partial H}{\partial T} \right)_p$	Heat capacity at constant pressure (J/K; $C_{p,m}$ =J/mol·K). $C_p > 0$ .
$\gamma \equiv \frac{C_p}{C_V}$	Heat capacity ratio. Unitless. Always $> 1$ for gases.
$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$	Thermal expansion coefficient. ( $K^{-1}$ ). $\alpha > 0$ for most materials.
$\kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$	Isothermal compressibility. (pressure $^{-1}$ ). $\kappa_T > 0$ , but note sign in definition. Things shrink at high pressure.
$\pi_T \equiv \left( \frac{\partial U}{\partial V} \right)_T$	Internal pressure (pressure units). Effectively, the <i>component</i> of the total pressure that is exclusively due to intermolecular forces is $-\pi_T$ . Zero for ideal gas; $\pi_T > 0$ for net attractive interactions and $\pi_T < 0$ for net repulsive interactions. Relevant to expansion into a vacuum (for example).

Note on internal pressure:

$$U(T, V) \longrightarrow dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \\ = \pi_T dV + C_V dT$$

Thus  $dU = C_V dT$  for  $dV = 0$  (constant volume);  $\pi_T$  is only apparent when the volume changes.

$\mu \equiv \left( \frac{\partial T}{\partial p} \right)_H$	Joule-Thompson coefficient. (K/pressure). Describes the change in temperature with respect to pressure when $dH = 0$ ( $U_i + p_i V_i = U_f + p_f V_f$ ). Zero for ideal gas. $\mu > 0$ means cooling on expansion. $\mu < 0$ means heating on expansion.
$\mu_T \equiv \left( \frac{\partial H}{\partial p} \right)_T = -\mu C_p$	Isothermal Joule-Thompson coefficient. (J/pressure). Can be positive or negative; sign is opposite $\mu$ . As a molar quantity: $\mu_{T,m} = -\mu C_{p,m}$ (J/mol·pressure).

Note on Joule-Thompson:

$$H(p, T) \longrightarrow dH = \left( \frac{\partial H}{\partial p} \right)_T dp + \left( \frac{\partial H}{\partial T} \right)_p dT \\ = \mu_T dp + C_p dT$$

Thus  $dH = C_p dT$  for  $dp = 0$  (constant pressure). The isothermal J-T coefficient  $\mu_T$  describes the amount of heat that must be supplied (or removed) to keep  $T$  constant, for a given change in pressure.

To see the connection to  $\mu$ , we apply the Euler chain rule to sub in for  $\mu_T$ :

$$dH = - \left( \frac{\partial H}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_H dp + \left( \frac{\partial H}{\partial T} \right)_p dT \\ = -C_p \mu dp + C_p dT$$