

Chapter 2

Equations of State

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2.2 Equation of State of an Ideal Gas

$$PV = \frac{m}{M}RT \quad (2.1)$$

m : mass of gas

M : molecular weight

R : universal constant

$$(8.314 \times 10^3 \frac{\text{J}}{\text{kilomole}\cdot\text{K}})$$

- Since $n \equiv \frac{m}{M}$ is the number of kilomoles of the gas, the equation of state of an ideal gas is

$$PV = nRT \quad (2.2)$$

2.2 Equation of State of an Ideal Gas

- In Equation (2.2) we note that the extensive variable V divided by n , the number of kilomoles of the gas, is the specific volume v .
- Thus the equation of state can be written $Pv = RT$
- The projections of the surface $f(P, v, T) = 0$ on the $P - v$ plane, $P - T$ plane, and the $v - T$ plane are shown in Figure 2.1

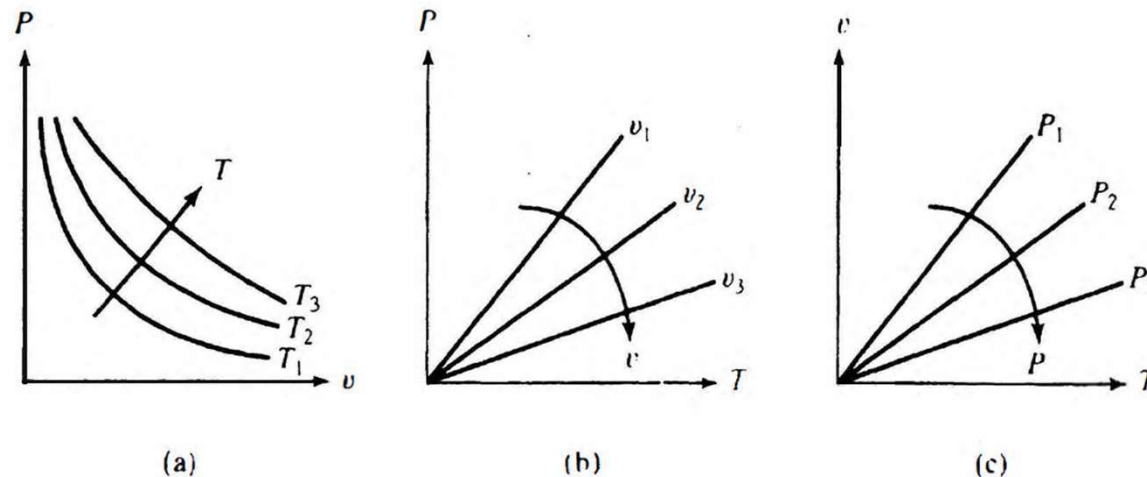


Figure 2.1 Diagrams for an ideal gas. (a) the isotherms are equilateral hyperbolae; (b) the isochores are straight lines; (c) the isobars are also straight lines.

2.3 Van Der Waals' Equation for a Real Gas

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (2.3)$$

a and *b*: characteristic constants

- The term $\frac{a}{v^2}$ arises from the intermolecular forces due to the overlap of electron clouds.
- The constant *b* takes into account the finite volume occupied by the molecules.
- Multiplication of Equation (2.3) by v^2 yields the equation

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0 \quad (2.4)$$

2.3 Van Der Waals' Equation for a Real Gas

- Equation (2.4) is a cubic equation in v with three roots, only one of which needs to be real.
- In Figure 2.2 some isotherms calculated from the van der Waals equation have been drawn.

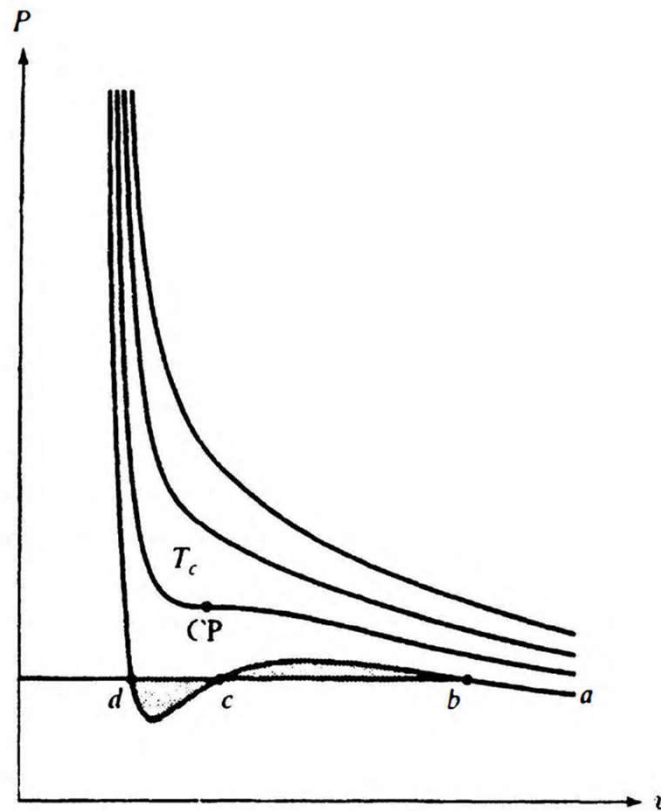


Figure 2.2 Isotherms for a Van Der Waals' gas.

2.4 $P - v - T$ Surfaces for Real Substances

- Figure 2.3 is a schematic diagram of the $P - v - T$ surface for a substance that contracts on freezing

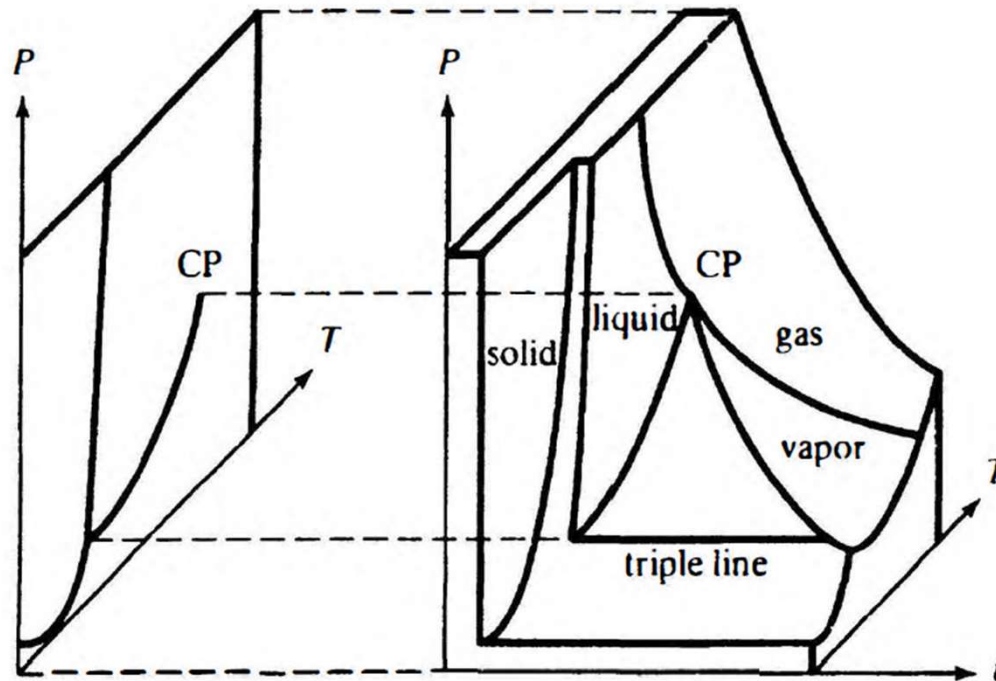


Figure 2.3 $P - v - T$ surface for a substance that contracts on freezing

2.4 $P - v - T$ Surfaces for Real Substances

- Notice the regions (solid, liquid, gas or vapor) in which the substance can exist in a single phase only.
- Elsewhere two phases can exist simultaneously in equilibrium, and along the so-called triple line, all three phases can coexist.

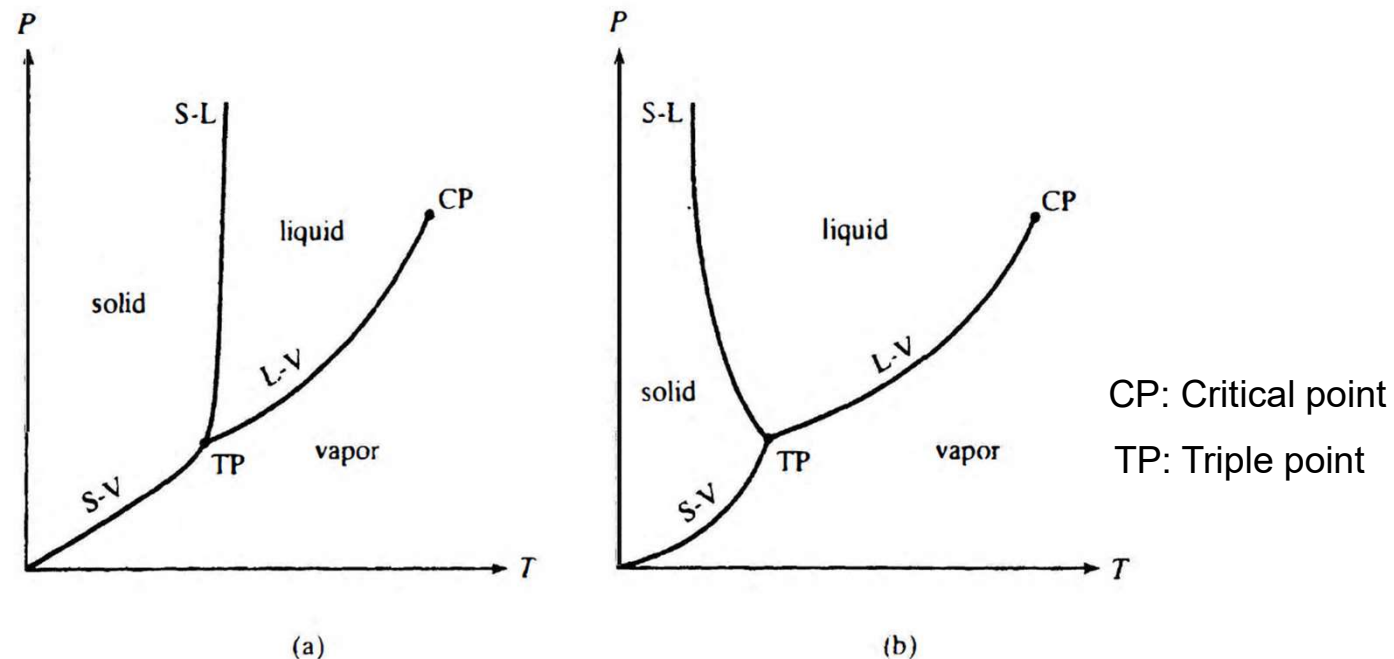


Figure 2.4 $P - T$ diagrams for (a) a substance that contracts on freezing; and (b) a substances that expands on freezing

2.5 Expansivity and Compressibility

- Suppose that the equation of state of a given substance is written in the form

$$v = v(T, P) \quad (2.5)$$

- Taking the differential, we obtain

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP \quad (2.6)$$

- The expansivity, or coefficient of volume expansion, is given by

$$\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \quad (2.7)$$

- This is the fractional change of volume resulting from a change in temperature, at constant pressure.

2.5 Expansivity and Compressibility

- Similarly, the isothermal compressibility is defined as

$$k \equiv -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (2.8)$$

- This is the fractional change in volume as the pressure changes, with the temperature held constant.
- The negative sign is used since the volume always decreases with increasing pressure (at constant temperature)
- For an ideal gas, $v = RT/P$

$$\beta = \frac{1}{v} \left(\frac{R}{P} \right) = \frac{1}{T} \quad (2.9)$$

$$k = -\frac{1}{v} \left(-\frac{RT}{P^2} \right) = \frac{1}{P} \quad (2.10)$$

2.7 Specific heat

- **Specific heat:** the amount of heat required to change a unit mass of a substance by one degree in temperature

$C_P, C_V \rightarrow$ The properties we can measure

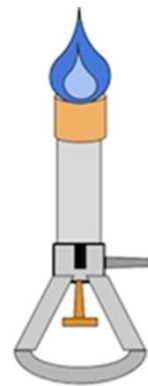
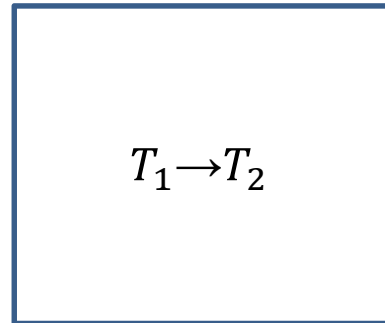
$$u = u(T, v) \quad (2.11)$$

$$du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{C_v} dT + \left(\frac{\partial u}{\partial v}\right)_T dv \quad (2.12)$$

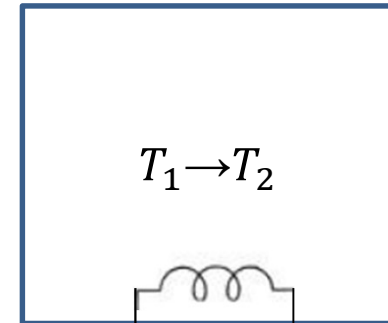
$$\begin{aligned} \delta Q &= \Delta U + \delta W \\ &= \Delta U + Pdv \\ &= \Delta U \end{aligned} \quad \begin{array}{l} \nearrow \\ \text{If there is no volume change} \\ \text{(constant } v\text{)} \end{array} \quad (2.13)$$

2.7 Specific heat

V constant



V constant



$$Q = i^2 R$$



Easier to measure *heat*
and *internal energy* in
difference

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v = \left(\frac{\partial Q}{\partial T} \right)_v \longrightarrow C_v \text{ can be measured}$$

2.7 Specific heat

$$\begin{aligned}h &\equiv u + pv \\ &= h(T, P)\end{aligned}\quad (2.14)$$

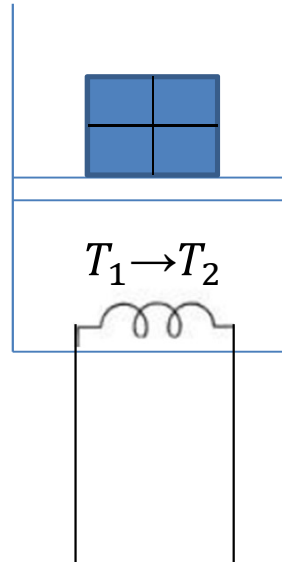
$$dh = \underbrace{\left(\frac{\partial h}{\partial T}\right)_P}_{C_P} dT + \left(\frac{dh}{dp}\right)_T dP \quad (2.15)$$

$$\begin{aligned}\delta Q)_{Idea} &= Tds = du + Pdv \\ &= dh - v dP\end{aligned}\quad (2.16)$$

If there is no pressure change
(constant P)

2.7 Specific heat

Constant pressure



Amount of heat added = Δh

$$C_P \equiv \left(\frac{\partial h}{\partial T} \right)_P = \left(\frac{\partial Q}{\partial T} \right)_P \longrightarrow C_P \text{ can be measured}$$

2.8 Maxwell equation

$$du = Tds - Pdv \quad (2.17)$$

$$u = u(s, v) \quad (2.18)$$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \quad (2.19)$$

T $-P$

$$\frac{\partial^2 U}{\partial v \partial s} = \left(\frac{\partial T}{\partial v}\right)_s = \frac{\partial^2 U}{\partial s \partial v} = -\left(\frac{\partial P}{\partial s}\right)_v \longrightarrow \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad (2.20)$$

2.8 Maxwell equation

$$J = \frac{\partial(P, v)}{\partial(T, s)} = 1$$

Jacobian

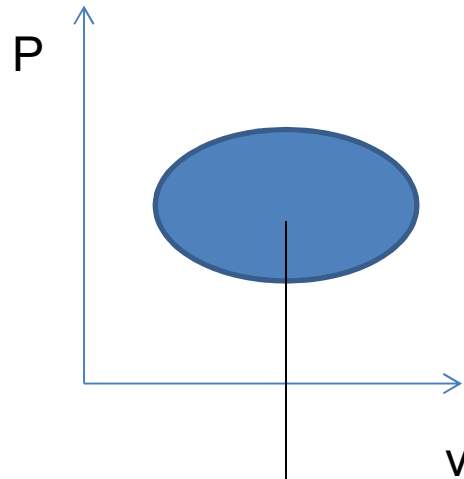
$$dxdy = rdrd\theta$$

$$x = r\cos\theta$$

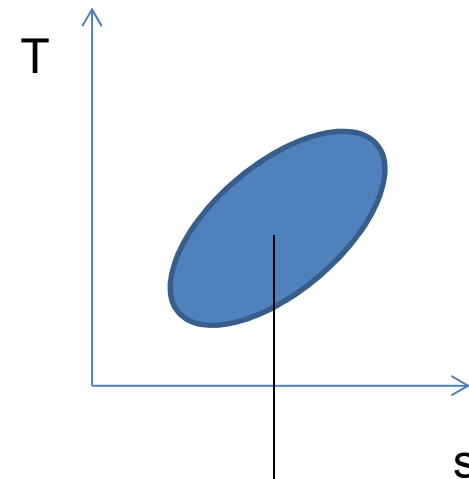
$$y = r\sin\theta$$

$$J = \frac{\partial(x, y)}{\partial(r, \theta)} = \det \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{vmatrix} = \begin{vmatrix} \cos\theta & -r\sin\theta \\ \sin\theta & r\cos\theta \end{vmatrix} = r(\cos^2\theta + \sin^2\theta) = r$$

$$\frac{\partial(T, s)}{\partial(v, s)} = \frac{\partial(P, v)}{\partial(v, s)} = -\frac{\partial(P, v)}{\partial(s, v)} = -\left(\frac{\partial P}{\partial s}\right)_v$$



W_{net}



W_{net}

2.9 Various equations of state

Cubic equation of state (EOS)

- Van der Waals EOS (1873)

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

- Peng-Robinson (PR) EOS (1976)

$$p = \frac{RT}{v - b} - \frac{a(T)}{v^2 + 2bv - b^2}$$

- Redlich-Kwong (RK) EOS (1949)

$$p = \frac{RT}{v - b} - \frac{a}{\sqrt{T} v (v + b)}$$

- Patel-Teja EOS (1982)

$$p = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (b + c)v - bc}$$

- Soave-Redlich-Kwong (SRK) EOS (1972)

$$p = \frac{RT}{v - b} - \frac{a(T)}{v (v + b)}$$

2.9 Various equations of state

Virial equation of state (EOS)

- BWR (Benedict–Webb–Rubin) Starling EOS (1970)

$$Z = \frac{pv}{RT} = 1 + \rho_r \left(E_1 - \frac{E_2}{T_r} - \frac{E_3}{T_r^3} + \frac{E_9}{T_r^4} - \frac{E_{11}}{T_r^5} \right) + \rho_r^2 \left(E_5 - \frac{E_6}{T_r} - \frac{E_{10}}{T_r^2} \right) + \rho_r^5 \left(\frac{E_7}{T_r} + \frac{E_{12}}{T_r^2} \right) + \frac{E_8 \rho_r^2}{T_r^3} (1 + E_4 \rho_r^2) \exp(-E_4 \rho_r^2) \quad E_i = a_i + \gamma_o b_i$$

- Lee-Kesler EOS (1975)

$$Z = \frac{pv}{RT} = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{c_4}{T_r^3 v_r^2} \left(\beta + \frac{\gamma}{v_r^2} \right) \exp \left(-\frac{\gamma}{v_r^2} \right)$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \quad D = d_1 + \frac{d_2}{T_r}$$

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)})$$

- MBWR EOS (1973, 1987)

$$p = \sum_{i=1}^9 a_i(T) \rho^i + \exp(-\delta^2) \sum_{i=10}^{15} a_i(T) \rho^{2i-17}$$

$$\delta = \frac{\rho}{\rho_r}$$

$$a_1 = RT$$

$$a_2 = b_1 T + b_2 T^{1/2} + b_3 + \frac{b_4}{T} + \frac{b_5}{T^2}$$

$$a_3 = b_6 T + b_7 + \frac{b_8}{T} + \frac{b_9}{T^2}$$

$$a_4 = b_{10} T + b_{11} + \frac{b_{12}}{T}$$

$$a_5 = b_{13}$$

$$a_6 = \frac{b_{14}}{T} + \frac{b_{15}}{T^2}$$

$$a_7 = \frac{b_{16}}{T}$$

$$a_8 = \frac{b_{17}}{T} + \frac{b_{18}}{T^2}$$

$$a_9 = \frac{b_{19}}{T^2}$$

$$a_{10} = \frac{b_{20}}{T^2} + \frac{b_{21}}{T^3}$$

$$a_{11} = \frac{b_{22}}{T^2} + \frac{b_{23}}{T^4}$$

$$a_{12} = \frac{b_{24}}{T^2} + \frac{b_{25}}{T^3}$$

$$a_{13} = \frac{b_{26}}{T^2} + \frac{b_{27}}{T^4}$$

$$a_{14} = \frac{b_{28}}{T^2} + \frac{b_{29}}{T^3}$$

$$a_{15} = \frac{b_{30}}{T^2} + \frac{b_{31}}{T^3} + \frac{b_{32}}{T^4}$$

2.9 Various equations of state

Multi-parameter equation of state (EOS)

- Helmholtz energy equation of state (EOS) for pure fluid

$$\alpha(\delta, \tau) = \frac{a(\rho, T)}{RT} = \frac{a^0(\rho, T) + a^r(\rho, T)}{RT} = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau)$$

Helmholtz energy

$$a = u - Ts$$

$$\alpha^0(\delta, \tau) = \frac{a^0(\rho, T)}{RT} = \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau} d\tau$$

$$\alpha^0(\delta, \tau) = a_1 + a_2 \tau + \ln \delta + (c_0 - 1) \ln \tau - \sum_{i=1}^{N_p} \frac{n_i \tau^{t_i}}{t_i (t_i - 1)} + \sum_{k=1}^{N_e} v_k \ln [1 - \exp(-u_k \tau / T_c)]$$

Departure function

$$\begin{aligned} \alpha^r(\delta, \tau) = & \sum_{k=1}^{K_p} n_k \delta^{d_k} \tau^{t_k} + \sum_{k=K_p+1}^{K_p+K_e} n_k \delta^{d_k} \tau^{t_k} \exp(-\delta^{l_k}) \\ & + \sum_{k=K_p+K_e+1}^{K_p+K_e+K_G} n_k \delta^{d_k} \tau^{t_k} \exp[-\eta_k (\delta - \epsilon_k)^2 - \beta_k (\tau - \gamma_k)^2] \\ & + \sum_{k=K_p+K_e+K_G+1}^{K_p+K_e+K_G+K_N} n_k \delta \Delta^{b_k} \psi \end{aligned}$$

$$\delta = \frac{\rho}{\rho_r} \quad \tau = \frac{T_r}{T}$$