

## Real gases

### Partition function of the ideal gas

For an ideal (Boltzmann) gas consisting of  $N$  indistinguishable molecules of mass  $m$ , we have

$$E = \sum_{i=1}^{3N} \varepsilon_i, \quad \varepsilon_i = \frac{p_i^2}{2m}$$

and

$$e^{-\beta E} = e^{-\beta \sum_{i=1}^{3N} \varepsilon_i} = e^{-\beta \varepsilon_1} e^{-\beta \varepsilon_2} e^{-\beta \varepsilon_3} \dots = \prod_i e^{-\beta \varepsilon_i},$$

The single-particle partition function (for  $N = 1$ ) is

$$z = \sum_i e^{-\beta \frac{p_i^2}{2m}} = \frac{1}{h^3} \left[ \int_{-\infty}^{\infty} e^{-\beta E(p_i)} d\Gamma_i \right]^3 = V \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2} = V n_Q = \frac{n_Q}{n}, \quad d\Gamma_i = dp_i dq_i \equiv \text{phase space}$$

where we replaced the sum over discrete states by an integral over the phase space.  $n_Q = \frac{1}{\lambda^3} = \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2}$  is called the “quantum concentration” and  $n = \frac{1}{V}$  is the concentration. The  $n_Q$  is the concentration associated with one particle in a cube of side  $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ .

For  $N$ -particles:

$$\begin{aligned} Z &= \frac{[z]^N}{N!} = \frac{V^N}{N!} \left( \frac{2\pi m}{h^2 \beta} \right)^{3N/2} \\ \Rightarrow F &= -k_B T \ln Z = -N k_B T \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi m}{\beta h^2} \right) \right] \\ \Rightarrow P &= \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} = \frac{1}{\beta} \frac{N}{V} \Rightarrow PV = N k_B T \end{aligned}$$

### Partition function of the real gases

In real gases, we must take into account the intermolecular forces and the finite dimension of the molecules. The intermolecular forces are of fairly short range and decrease rapidly with increasing the distance between molecules (atoms). For real gases

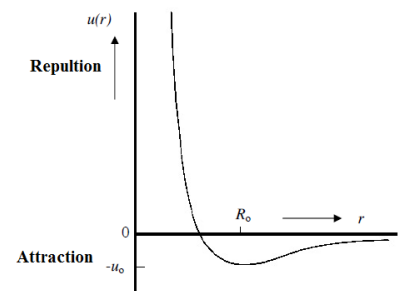
$$H(\mathbf{p}, \mathbf{r}) = E(\mathbf{p}) + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N),$$

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{j>i} U(\mathbf{r}_{ij})$$

$$Z = Z_p Z_U = \left\{ \frac{V^N}{N! h^{3N}} \left[ \int_{-\infty}^{\infty} e^{-\beta \frac{p_i^2}{2m}} dp_i \right]^{3N} \right\} \left\{ \frac{1}{V^N} \left[ \int e^{-\beta U(\mathbf{r})} d\mathbf{r} \right] \right\}$$

where  $Z_U$  is the configurational partition function of the gas.  $Z_U = 1$  for ideal gas.

$$Z_U = \frac{1}{V^N} \left[ \int e^{-\beta U(\mathbf{r})} d\mathbf{r} \right] = \frac{1}{V^N} \left[ \int \prod_{i>j} e^{-\beta U(\mathbf{r}_{ij})} \prod_{i=1}^N d^3 r_i \right]$$



Define the Mayer's function as:

$$f_{ij} = e^{-\beta U(r_{ij})} - 1$$

which measure the degree of imperfection of the gas and it is equal to zero for ideal gases.

$$Z_U = \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \left[ (1 + f_{12})(1 + f_{13}) \cdots (1 + f_{N-1,N}) \right] = \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \left[ 1 \right]$$

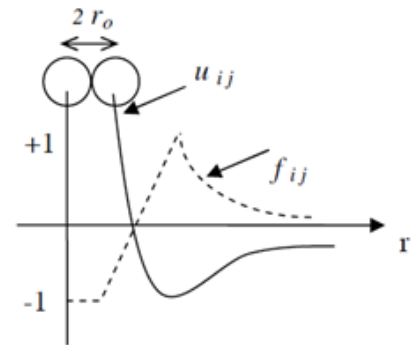


Figure 1: Intermolecular potential energy and Mayer's function.

### Cluster expansion

The above expansion is called the "Virial\*" or "cluster" expansion.

The first term is used in case of the ideal gas and the second term will leads to:

$$B_2 = V^{-N} \int \sum_{j>i} f_{ij} d^3r_1 \cdots d^3r_N = V^{-N} \left[ \frac{1}{2} N(N-1) \right] \int f_{12} d^3r_1 d^3r_2 \underbrace{d^3r_3 \cdots d^3r_N}_{V^{N-2}}$$

The above square bracket gives the number of ways that we can choose pairs of molecules, and for it gives

$$\sum_{j>i} = \frac{1}{2} N(N-1) = \frac{N^2}{2} \text{ if } N \gg 1 \text{ which is the normal case.}$$

$$B_2 \approx V^{-N} \frac{N^2}{2} V^{N-2} \int f_{12} d^3r_1 d^3r_2$$

\*The word "virial" is related to the Latin word for force. Clausius named a certain function of the force between molecules "the virial of force." This name was subsequently taken over for the virial expansion because the terms in that expansion can be calculated from the forces between the molecules.

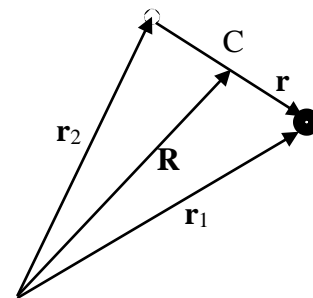
### The two body integrals

The two body integrals could be solved by using the transformation

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (\text{relative}), \quad \mathbf{R} = \frac{(\mathbf{r}_1 + \mathbf{r}_2)}{2} \quad (\text{center})$$

Then

$$d^3r d^3R = \begin{vmatrix} \frac{\partial r}{\partial r_1} = 1 & \frac{\partial r}{\partial r_2} = -1 \\ \frac{\partial R}{\partial r_1} = \frac{1}{2} & \frac{\partial R}{\partial r_2} = \frac{1}{2} \end{vmatrix} d^3r_1 d^3r_2 = d^3r_1 d^3r_2.$$



Using  $d^3R = V$ , and

$$B_2 = V^{-2} \frac{N^2}{2} \int (e^{-\beta u(r)} - 1) d\mathbf{r} d\mathbf{R} = \frac{N^2}{2V} I_2$$

where  $I_2 = \int (e^{-\beta u(r)} - 1) d\mathbf{r}$  proportional to the volume of the molecule. The partition function  $Z_U$  will be:

$$Z_U = 1 + N(x) + \cdots \approx (1+x)^N, \quad x = \frac{NI_2}{2V} \ll 1$$

For single particle:

$$\ln(Z_U) = \ln(1+x) = x, \quad x \ll 1$$

We used the expansion  $\ln[1-x] \approx -x$ , where  $x \ll 1$ . Consequently, we have

$$\ln Z_P = N[\ln V + f(T)], \quad \ln Z_U = \left[ \frac{NI_2}{2V} \right]$$

$$P = \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} = \frac{1}{\beta} \left( \frac{\partial \ln Z_P}{\partial V} \right)_{T,N} + \frac{1}{\beta} \left( \frac{\partial \ln Z_U}{\partial V} \right)_{T,N} = \frac{Nk_B T}{V} - k_B T \left[ \frac{N^2 I_2}{2V^2} \right] = \frac{Nk_B T}{V} \left( 1 - \frac{NI_2}{2V} \right)$$

In general

$$P = \frac{Nk_B T}{V} \left[ 1 + \frac{N}{V} B(T) + \left( \frac{N}{V} \right)^2 C(T) + \dots \right]$$

The coefficient,  $B(T) = -\frac{I_2}{2}$ ,  $I_2 = \int (e^{-\beta u(r)} - 1) dr$  is a function of temperature and is called the "second virial" coefficient.  $C(T)$  is called the "third virial" coefficient, and so on. The expansion is, in principle, an infinite series, and as such should be valid for all isotropic substances. In practice, however, terms above the third virial coefficient are rarely used in chemical thermodynamics.

### Notice that

- 1- We have set the quantity  $PV = Nk_B T$  equal to  $Z$ . This quantity ( $Z$ ) is called the "compression factor." It is a useful measure of the deviation of a real gas from an ideal gas. For an ideal gas the compression factor is equal to 1.
- 2- The virial expansion breaks down not only at high densities, but also at low temperatures. This is suggested by the divergences in  $B(T)$  as  $T \rightarrow 0$ , and reflects the fact that in the presence of attractive interactions the particles can lower their energy at low temperatures by condensing into a liquid state.

## Applications:

### I. Rigid sphere model

The Model of hard sphere is given by (see figure 1):

$$u(r) = \begin{cases} \infty, & 0 \leq r \leq 2r_0 \\ 0, & r > 2r_0 \end{cases}$$

where  $r_0$  is the radius of the molecule. Find the second virial coefficient.

**Answer:** The second virial coefficient could be calculated as follows:

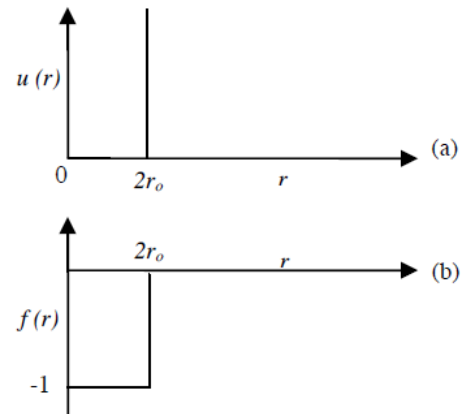
$$f_{ij} = e^{-\beta U(r_{ij})} - 1 = \begin{cases} -1, & 0 \leq r \leq 2r_0 \\ 0, & r > 2r_0 \end{cases}$$

$$B(T) = -\frac{I_2}{2} = -\frac{1}{2} \int_0^\infty (e^{-\beta u(r)} - 1) d^3 r = -\frac{4\pi}{2} \left[ \int_0^{2r_0} (-1) r^2 dr + \int_{2r_0}^\infty (0) r^2 dr \right]$$

$$\approx 2\pi \left[ \int_0^{2r_0} r^2 dr \right] = \frac{16\pi}{3} r_0^3 = b,$$

The constant  $b$  equals to  $4V_o$ , where  $V_o = \frac{4}{3}\pi r_o^3$  is the volume of the molecule. Thus, the equation of state for a gas of rigid sphere is

$$P = \frac{Nk_B T}{V} \left[ 1 + \frac{N}{V} b + \dots \right]$$



Next, estimate the magnitude of  $\frac{N}{V}b$  for air at room temperature and pressure. The volume of a molecule is  $\sim 10^{-23} \text{ cm}^3$ , and at STP,  $\rho = \frac{N}{V} \cong 3 \times 10^{20} \text{ molecules/cm}^3$ . Thus,  $\frac{N}{V}b \cong 10^{-3}$ . Higher terms in  $\rho^2, \rho^3, \dots$  can be shown to be smaller. Thus,

$$PV \cong \overset{=PV}{Nk_B T} + Nk_B T \frac{N}{V} b = Nk_B T + PN \overset{4V_o}{b}$$

Hence,

$$P [V - 4NV_o] \approx Nk_B T$$

Evidently, the equation of state is the same as for an ideal gas, if the container volume is replaced by a reduced volume obtained by subtracting four times the volume of all the molecules, i.e.  $V_{red} = V - 4NV_o$ .

## II. van der Waals Gas

For van der Waals gas, we will use the potential:

$$u(r) = \begin{cases} \infty, & 0 \leq r \leq 2r_o \\ U, & r > 2r_o \end{cases}$$

where  $U$  is a function of  $r$ . Find the second virial coefficient.

**Answer:** The second virial coefficient could be calculated as follows:

$$f_{ij} = e^{-\beta U(r_{ij})} - 1 = \begin{cases} -1, & 0 \leq r \leq 2r_o \\ -\beta U, & r > 2r_o \end{cases}$$

$$\begin{aligned} B(T) &= -\frac{I_2}{2} = -\frac{1}{2} \int_0^\infty (e^{-\beta u(r)} - 1) d^3r = -\frac{4\pi}{2} \left[ \int_0^{2r_o} (-1) r^2 dr + \int_{2r_o}^\infty (-\beta U) r^2 dr \right] \\ &\approx 2\pi \left[ \int_0^{2r_o} r^2 dr + \int_{2r_o}^\infty r^2 \beta U dr \right], \\ &= b - \frac{a}{k_B T} \end{aligned}$$

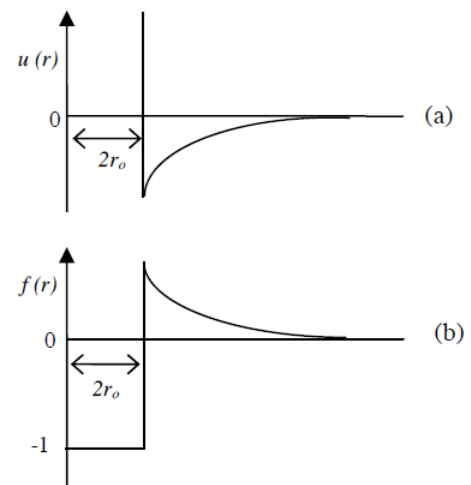
$$\Rightarrow b = 4V_o = 4 \left( \frac{4}{3} \pi r_o^3 \right), \quad a = -2\pi \int_{2r_o}^\infty r^2 \beta U dr$$

$a$  comes from the long range weak attraction force between the molecules,  $b$  comes from the volume  $V_o$  of the molecules. Finally

$$\begin{aligned} P &= \frac{NkT}{V} \left[ 1 + \frac{N}{V} (b - a/kT) \right] = \frac{NkT}{V} \left[ 1 + \frac{N}{V} b \right] - \frac{N^2}{V^2} a \\ &\approx \frac{NkT}{V} \left[ 1 - \frac{N}{V} b \right]^{-1} - \frac{N^2}{V^2} a \end{aligned}$$

Then

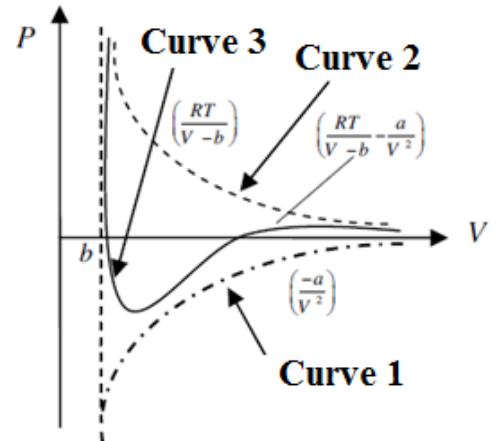
$$\left( P + \frac{N^2}{V^2} a \right) (V - Nb) = NRT$$



**Figure description**

**Curve 1** for attraction forces, **Curve 2** for the repulsive force, **Curve 3** is the resultant.

The equation is satisfied with fairly good accuracy by many real gases, especially for large value of  $v = V/N$ . The coefficients  $a$  and  $b$  are called van der Waals constants. They are given in the following table for several real gases.



Substance	$a,$ $\text{Nm}^4\text{kg}^{-2}\text{mole}^{-2}$	$b,$ $\text{m}^3\text{kg}^{-1}\text{mole}^{-1}$
Helium	$3.446 \times 10^3$	0.02370
Hydrogen	$2.468 \times 10^4$	0.02661
Nitrogen	$1.404 \times 10^5$	0.03913
Sulfur dioxide	$6.781 \times 10^5$	0.05636
Water	$5.519 \times 10^5$	0.03049

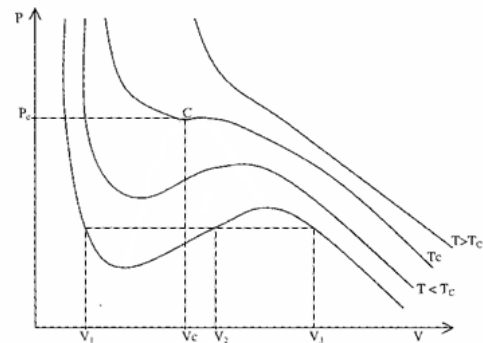
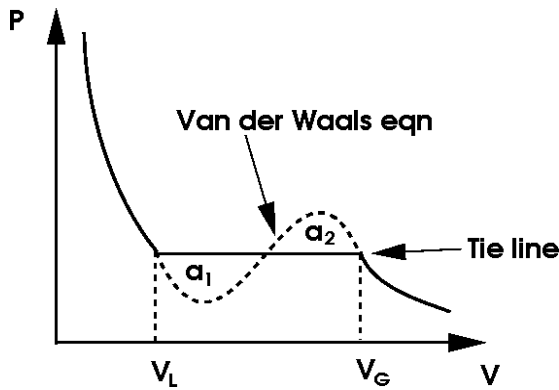
Simplify van der Waal's equation, one has:

$$\left(P + \frac{1}{v^2}a\right)(v-b) = RT \Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2}, \quad v = V/N$$

$$\left(Pv + \frac{1}{v}a\right) - \left(\frac{ab}{v^2} + bP\right) = RT$$

Or

$$Pv^3 - (Pb + RT)v^2 + a(v-b) = 0$$



**Comments:**

- 1-  $a$  and  $b$  are constants. " $a$ " is used to correct for the intermolecular attractions and " $b$ " is used to correct for the finite size of the molecules, it is the excluded volume due to the finite size of the molecules.
- 2- It is a cubic equation in  $v$  with three roots, only one of which need to be real.
- 3- As  $T$  increases.  $T > T_c$  the curves approach  $PV = \text{constant}$ . i.e. the ideal gas law.
- 4- For  $T < T_c$  there is a local maximum and minimum value of  $P$ .
- 5- Between the two type of curves is a curve having an inflection point  $C$   $P$ . the so called critical point,  $T = T_c$
- 6- At  $T_c$  one can have

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

with the conditions  $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$ . It is easy to find  $v_c = 3b$ ,  $P_c = \frac{2}{27b^2}$ ,  $T_c = \frac{8a}{27Rb}$ .

which give  $P_c V_c = \frac{3}{8} RT_c$  for a van der Waals' gas at the critical point.

### 7. Derivatives

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} \Rightarrow \left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$$

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}, \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4},$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P - \frac{a}{v^2} + \frac{2ab}{v^3}} = \frac{Rv^3(v-b)}{RTv^3 - 2a(v-b)^2},$$

$$Pv^3 - (bP + RT)v^2 + av - ab = 0 \Rightarrow \\ v^3 dP + 3v^2 P dv - (bdP + RdT)v^2 - 2v(bP + RT)dv + adv = 0$$

### 8- Internal energy

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P = \frac{nR}{V-nb} - \left(\frac{nR}{V-nb} - \frac{an^2}{V^2}\right) \Rightarrow \Delta U = \int_{V_i}^{V_f} \frac{an^2}{V^2} dV = an^2 \left(\frac{1}{V_i} - \frac{1}{V_f}\right)$$

### 9. Work done

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nR}{V-nb} dV - \int_{V_i}^{V_f} \frac{an^2}{V^2} dV \\ = nRT \ln \left(\frac{V_f - nb}{V_i - nb}\right) + an^2 \left(\frac{1}{V_f} - \frac{1}{V_i}\right)$$

### 10. Heat

$$Q = \Delta u + W$$

### 11- Putting $dP = 0$ : Volume expansion coefficient

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{\left[3Pv - 2(bP + RT) + \frac{a}{v}\right]} = \frac{R}{Pv - \frac{a}{v} + \frac{2ab}{v^2}} \\ = \frac{1}{T} \left(1 - \frac{2a}{RTv} + \frac{bP}{RT} + \frac{3ab}{RTv^2}\right)^{-1} \\ \rightarrow \frac{1}{T} \text{ (as } a \rightarrow 0, \text{ and } b \rightarrow 0)$$

### 12- Putting $dT = 0$ : compressibility coefficient

$$\begin{aligned}\kappa &= -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = \frac{(v-b)}{\left[ 3Pv - 2(bP + RT) + \frac{a}{v} \right]} = \frac{(v-b)}{Pv - \frac{a}{v} + \frac{2ab}{v^2}} \\ &= \frac{1}{P} \left( 1 - \frac{b}{v} \right) \left( 1 - \frac{2a}{Pv^2} + \frac{2ab}{Pv^3} \right)^{-1} \\ &\rightarrow \frac{1}{P} \text{ (as } a \rightarrow 0, \text{ and } b \rightarrow 0)\end{aligned}$$

### 13- Specific heat

$$\begin{aligned}c_p - c_v &= \left[ P + \left( \frac{\partial U}{\partial v} \right)_T \right] \left( \frac{\partial v}{\partial T} \right)_P = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial v}{\partial T} \right)_P = \frac{R}{\left[ 1 - \frac{2a}{RTv^3} (v-b)^2 \right]} \\ &= \left( \frac{RT}{v-b} \right) \frac{(vR)}{\left[ 3Pv - 2(bP + RT) + \frac{a}{v} \right]} \\ &= R + R \left( \frac{2a}{Pv^3} - \frac{2ab}{Pv^3} \right) \left( 1 - \frac{a}{Pv^2} + \frac{2ab}{Pv^3} \right)^{-1} \\ &\rightarrow R \text{ (as } a \rightarrow 0, \text{ and } b \rightarrow 0)\end{aligned}$$

Note:

$$\begin{aligned}c_p &= T \left( \frac{\partial S}{\partial T} \right)_v \Rightarrow \left( \frac{\partial c_p}{\partial v} \right)_T = \left[ \frac{\partial}{\partial v} \left\{ T \left( \frac{\partial S}{\partial T} \right)_v \right\} \right]_T = T \left( \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial v} \right)_T \right)_v \\ &= T \left( \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial T} \right)_v \right)_v = T \left( \frac{\partial^2 P}{\partial T^2} \right)_v = 0\end{aligned}$$

Which implies the specific heat is P and v independent. It is T dependent.

### 14. Joule coefficient

$$\begin{aligned}\eta &= \left( \frac{\partial T}{\partial V} \right)_U = -\frac{1}{c_v} \left( \frac{\partial U}{\partial v} \right)_T = \frac{1}{c_v} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_v \right] \\ &= \frac{1}{c_v} \left[ \left( \frac{RT}{v-b} - \frac{a}{v^2} \right) - T \left( \frac{a}{(v-b)^2} \right) \right] = -\frac{a}{c_v v^2} \\ &\rightarrow 0 \text{ (as } a \rightarrow 0)\end{aligned}$$

### 15. Joule-Thomson coefficient

$$\begin{aligned}\mu &= \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{c_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_P - v \right] \\ &= \frac{v}{c_p} \left[ \frac{2a(v-b)^2 - RTbv^2}{RTv^3 - 2a(v-b)^2} \right] \\ &\rightarrow 0 \text{ (as } a \rightarrow 0, \text{ and } b \rightarrow 0)\end{aligned}$$

### 16. Enthalpy

$$Pv = \frac{RTv}{v-b} - \frac{a}{v} \Rightarrow$$
$$\Delta(Pv) = (P_2v_2 - P_1v_1) = RTb \left( \frac{1}{v_2-b} - \frac{1}{v_1-b} \right) - \left( \frac{a}{v_2} - \frac{a}{v_1} \right)$$
$$\Delta H = \Delta u + \Delta(Pv) = RTb \left( \frac{1}{v_2-b} - \frac{1}{v_1-b} \right) - 2 \left( \frac{a}{v_2} - \frac{a}{v_1} \right)$$
$$\rightarrow 0 \text{ (as } a \rightarrow 0 \text{)}$$