
Thermodynamic Properties of a PVT System

The thermodynamic properties of a PVT system are completely determined if the equation of state and the functional form of the molar internal energy u are known.

Ideal Gas

For the ideal gas, we have

$$Pv = RT \quad (1)$$

and

$$u = \frac{3}{2}RT \quad (2)$$

Hence,

$$h = u + Pv = \frac{5}{2}RT \quad (3)$$

$$c_v = \left(\frac{\partial q}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{3}{2}R \quad (4)$$

$$c_p = \left(\frac{\partial q}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p = \frac{5}{2}R \quad (5)$$

In general, (4) gives

$$(ds)_v = \frac{c_v}{T} dT$$
$$s = \int dT \frac{c_v}{T} + C_1(v) \quad (6)$$

where $C_1(v)$ is an arbitrary function of v .

If c_v is a constant, (6) becomes

$$s = c_v \ln T + C_1(v)$$
$$= \frac{3}{2}R \ln T + C_1(v) \quad [\text{For the Ideal gas.}] \quad (7)$$

Similarly, (5) gives

$$(ds)_p = \frac{c_p}{T} dT$$
$$s = \int dT \frac{c_p}{T} + C_2(P) \quad (8)$$

where $C_2(P)$ is an arbitrary function of P .

If c_p is a constant,

$$s = c_p \ln T + C_2(P)$$
$$= \frac{5}{2}R \ln T + C_2(P) \quad [\text{For the Ideal gas.}] \quad (9)$$

Now, $T \left(\frac{\partial s}{\partial T}\right)_p$ gives

$$\begin{aligned}
c_p &= c_v + T \left(\frac{\partial v}{\partial T} \right)_p \frac{dC_1}{dv} \\
&= c_v + T \alpha_p \frac{dC_1}{dv} & [\alpha_p = \left(\frac{\partial v}{\partial T} \right)_p = \text{coefficient of thermal expansion.}] \\
&= \frac{3}{2}R + T \alpha_p \frac{dC_1}{dv} = \frac{5}{2}R & [\text{For the Ideal gas.}]
\end{aligned} \tag{10}$$

For the ideal gas, (1) gives

$$\alpha_p = \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{P} = \frac{v}{T} \tag{11}$$

(10) then becomes

$$v \frac{dC_1}{dv} = c_p - c_v = R$$

$$\begin{aligned}
\rightarrow C_1(v) &= (c_p - c_v) \ln v + \text{const} \\
&= R \ln v + \text{const}
\end{aligned} \tag{12}$$

(7) then gives

$$\begin{aligned}
s &= c_v \ln T + (c_p - c_v) \ln v + \text{const} \\
&= s_0 + \ln \left[\left(\frac{T}{T_0} \right)^{c_v} \left(\frac{v}{v_0} \right)^{c_p - c_v} \right] \\
&= s_0 + R \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \frac{v}{v_0} \right]
\end{aligned} \tag{13}$$

where

$$s_0 = s \Big|_{T=T_0, v=v_0}$$

(13) is just the Sackur-Tetrode equation [see Ex.2.3 of §2.E] with $s_0 = \frac{5}{2}R = c_p$.

From the molar Gibbs-Duhem equation (2.65),

$$d\mu = -s dT + v dP \tag{14}$$

we have

$$\begin{aligned}
(d\mu)_p &= -s dT \\
&= -\left\{ s_0 + \ln \left[\left(\frac{T}{T_0} \right)^{c_v} \left(\frac{v}{v_0} \right)^{c_p - c_v} \right] \right\}_p dT & [(13) \text{ used.}] \\
&= -\left\{ s_0 + \ln \left[\left(\frac{T}{T_0} \right)^{c_p} \left(\frac{P_0}{P} \right)^{c_p - c_v} \right] \right\}_p dT & [(1) \text{ used.}]
\end{aligned}$$

Using the *Mathematica* code

$$\begin{aligned}
&\int \left(s\theta + \text{Log} \left[\left(\frac{T}{T\theta} \right)^{cP} \left(\frac{P\theta}{P} \right)^{cP - cV} \right] \right) dT \\
&T \left(-cP + s\theta + \text{Log} \left[\left(\frac{P\theta}{P} \right)^{cP - cV} \left(\frac{T}{T\theta} \right)^{cP} \right] \right)
\end{aligned}$$

we have

$$\mu = -T \left\{ s_0 - c_p + \ln \left[\left(\frac{P_0}{P} \right)^{c_p - c_v} \left(\frac{T}{T_0} \right)^{c_p} \right] \right\} + C_3(P)$$

$$= -T \ln \left[\left(\frac{P_0}{P} \right)^{c_p - c_v} \left(\frac{T}{T_0} \right)^{c_p} \right] + C_3(P) \quad [s_0 = c_p] \quad (15)$$

where $C_3(P)$ is an arbitrary function of P .

$\left(\frac{\partial (15)}{\partial P} \right)_T$ gives

$$\begin{aligned} \left(\frac{\partial \mu}{\partial P} \right)_T &= T \frac{c_p - c_v}{P} + \frac{dC_3}{dP} \\ &= v \quad [(14) \text{ used. }] \\ &= \frac{RT}{P} \quad [(1) \text{ used. }] \end{aligned} \quad (16)$$

Hence,

$$\frac{dC_3}{dP} = (R - c_p + c_v) \frac{T}{P} = 0$$

→ $C_3 = \text{const.}$

(15) thus becomes

$$\mu = \mu_0 - T \ln \left[\left(\frac{P_0}{P} \right)^{c_p - c_v} \left(\frac{T}{T_0} \right)^{c_p} \right] \quad (17)$$

where

$$\mu_0 = \mu \Big|_{T=T_0, P=P_0}$$

Using (1), (13) & (16), we have

$$\begin{aligned} TS - PV + \mu &= T \left\{ s_0 + \ln \left[\left(\frac{T}{T_0} \right)^{c_v} \left(\frac{V}{V_0} \right)^{c_p - c_v} \right] \right\} - RT \\ &\quad - T \left\{ s_0 - c_p + \ln \left[\left(\frac{P_0}{P} \right)^{c_p - c_v} \left(\frac{T}{T_0} \right)^{c_p} \right] \right\} \\ &= (c_p - R) T \quad [(1) \text{ used to cancel the two log terms. }] \\ &= \frac{3}{2} RT \quad [\text{For the Ideal gas.}] \\ &= u \quad [(2) \text{ used. }] \end{aligned} \quad (18)$$

thus recovering the molar fundamental equation (2.63) of §2.E.

van der Waals Fluid

The van der Waals fluid obeys the equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad (19a)$$

In terms of the normalized variables

$$\bar{x} = \frac{x}{x_c} \quad x = P, T, v$$

where

$$P_c = \frac{a}{27b^2} \quad v_c = 3b \quad T_c = \frac{8a}{27bR}$$

(19a) becomes

$$\bar{P} = \frac{8\bar{T}}{3\bar{V}-1} - \frac{3}{\bar{V}^2} \quad (19)$$

Since the pressure term $-\frac{a}{V^2}$ or $-\frac{3}{\bar{V}^2}$ is due to the attractive interaction between the fluid particles, we can write the molar internal energy as

$$\begin{aligned} u &= \frac{3}{2}RT + \int dV \frac{a}{V^2} \\ &= \frac{3}{2}RT_c \bar{T} + P_c V_c \int d\bar{V} \frac{3}{\bar{V}^2} \\ &= \frac{3}{2}RT_c \bar{T} - 3 \frac{P_c V_c}{\bar{V}} \\ &= \frac{3}{2}RT_c \left(\bar{T} - \frac{3}{4\bar{V}} \right) \end{aligned} \quad (20)$$

where

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

was used. At the critical point

$$u_c = \frac{3}{8}RT_c = P_c V_c = \frac{a}{9b}$$

Using the kinetic energy at the critical point, $\epsilon_c = \frac{3}{2}RT_c$, as the unit of energy, we have

$$\bar{u} \equiv \frac{u}{\epsilon_c} = \frac{2u}{3RT_c} = \bar{T} - \frac{3}{4\bar{V}} \quad (\bar{u}_c = \frac{1}{4}) \quad (21)$$

The normalized molar enthalpy is therefore

$$\begin{aligned} \bar{h} \equiv \frac{h}{\epsilon_c} &= \bar{u} + \frac{2P_c V_c}{3RT_c} \bar{P} \bar{V} \\ &= \bar{u} + \frac{1}{4} \bar{P} \bar{V} \\ &= \bar{T} - \frac{3}{4\bar{V}} + \frac{1}{4} \bar{P} \bar{V} \quad (\bar{h}_c = \frac{1}{2}) \end{aligned} \quad (22)$$

Note that as $\bar{V} \rightarrow \infty$, the gas becomes ideal:

$$\bar{u} \rightarrow \bar{T} \quad \bar{P} \bar{V} = \left(\frac{8\bar{T}}{3\bar{V}-1} - \frac{3}{\bar{V}^2} \right) \bar{V} \rightarrow \frac{8\bar{T}}{3} \quad \bar{h} \rightarrow \frac{5}{3} \bar{T} \quad (23)$$

Using (21) and (22), we have

$$c_V = \frac{3}{2}R \left(\frac{\partial \bar{u}}{\partial \bar{T}} \right)_{\bar{V}} = \frac{3}{2}R \quad [\text{Same as the ideal gas.}] \quad (24)$$

$$\begin{aligned} c_P &= \frac{3}{2}R \left(\frac{\partial \bar{h}}{\partial \bar{T}} \right)_{\bar{P}} = \frac{3}{2}R \left[1 + \frac{1}{4} \left(\frac{3}{\bar{V}^2} + \bar{P} \right) \left(\frac{\partial \bar{V}}{\partial \bar{T}} \right)_{\bar{P}} \right] \\ &= \frac{3}{2}R \left[1 + \frac{2\bar{T}}{3\bar{V}-1} \left(\frac{\partial \bar{V}}{\partial \bar{T}} \right)_{\bar{P}} \right] \quad [(19) \text{ used.}] \end{aligned} \quad (25)$$

Now, $\left(\frac{\partial (19)}{\partial \bar{P}} \right)_{\bar{T}}$ gives

$$\begin{aligned} \left(\frac{\partial \bar{P}}{\partial \bar{v}}\right)_T &= -\frac{24\bar{T}}{(3\bar{v}-1)^2} + \frac{6}{\bar{v}^3} \\ &= -\frac{6[4\bar{T}\bar{v}^3 - (3\bar{v}-1)^2]}{(3\bar{v}-1)^2\bar{v}^3} \end{aligned} \quad (26)$$

Thus, $\left(\frac{\partial (19)}{\partial \bar{T}}\right)_{\bar{P}}$ gives

$$\begin{aligned} 0 &= \frac{8}{3\bar{v}-1} - \left(\frac{\partial \bar{P}}{\partial \bar{v}}\right)_T \left(\frac{\partial \bar{v}}{\partial \bar{T}}\right)_{\bar{P}} \\ \rightarrow \left(\frac{\partial \bar{v}}{\partial \bar{T}}\right)_{\bar{P}} &= \frac{3\bar{v}-1}{8\left(\frac{\partial \bar{P}}{\partial \bar{v}}\right)_T} = -\frac{(3\bar{v}-1)^3\bar{v}^3}{48[4\bar{T}\bar{v}^3 - (3\bar{v}-1)^2]} \end{aligned} \quad (27)$$

(25) then becomes

$$c_P = \frac{3}{2}R \left[1 - \frac{(3\bar{v}-1)^2\bar{v}^3\bar{T}}{24[4\bar{T}\bar{v}^3 - (3\bar{v}-1)^2]} \right] \quad (28)$$

Since c_v is a constant, we have [c.f. (7)]

$$\begin{aligned} c_v &= \bar{T} \left(\frac{\partial s}{\partial \bar{T}} \right)_{\bar{v}} \\ \rightarrow s &= \frac{3}{2}R \ln \bar{T} + C_1(\bar{v}) \end{aligned} \quad (29)$$

where $C_1(\bar{v})$ is an arbitrary function of \bar{v} . Hence,

$$c_P = \bar{T} \left(\frac{\partial s}{\partial \bar{T}} \right)_{\bar{P}} = \frac{3}{2}R + \bar{T} \left(\frac{\partial \bar{v}}{\partial \bar{T}} \right)_{\bar{P}} \frac{dC_1}{d\bar{v}} \quad (30)$$

Comparing (30) with (25) gives

$$\begin{aligned} \frac{dC_1}{d\bar{v}} &= \frac{3R}{3\bar{v}-1} \\ \rightarrow C_1(\bar{v}) &= R \ln(3\bar{v}-1) + \text{const} \end{aligned} \quad (31)$$

(29) thus becomes

$$\begin{aligned} s &= \frac{3}{2}R \ln \bar{T} + R \ln(3\bar{v}-1) + \text{const} \\ &= s_0 + R \ln \left[\left(\frac{\bar{T}}{\bar{T}_0} \right)^{3/2} \left(\frac{3\bar{v}-1}{3\bar{v}_0-1} \right) \right] \end{aligned} \quad (32)$$

$$= s_0 + R \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{v-b}{v_0-b} \right) \right] \quad [v_c = 3b] \quad (32a)$$

where

$$s_0 = s \Big|_{\bar{T}=\bar{T}_0, \bar{v}=\bar{v}_0}$$

Thus, the latent heat of vaporization is

$$\begin{aligned} \Delta h_{lg} &= T(s_g - s_l) \\ &= RT \ln \left[\frac{v_g(T) - b}{v_l(T) - b} \right] \end{aligned} \quad (33)$$

where the vapor and liquid phase volumes, $v_g(T)$ and $v_l(T)$, are given by the largest and smallest roots of the vdW equation (3.41) for $P = P_{\text{coex}}(T)$, respectively [see §3.D.4].

The Clausius-Clapeyron equation [see (3.14) of §3.D.2] thus becomes

$$\frac{dP_{\text{coex}}}{dT} = \frac{R}{v_g(T) - v_l(T)} \ln \left[\frac{v_g(T) - b}{v_l(T) - b} \right] \quad (33a)$$

Now, as T approaches T_c , $v_g(T)$ becomes close to $v_l(T)$, (33a) then simplifies to

$$\begin{aligned} \frac{dP_{\text{coex}}}{dT} &= \frac{R}{v_g(T) - v_l(T)} \ln \left[1 + \frac{v_g(T) - v_l(T)}{v_l(T) - b} \right] \\ &\approx \frac{R}{v_g(T) - v_l(T)} \left[\frac{v_g(T) - v_l(T)}{v_l(T) - b} + \dots \right] \\ &\approx \frac{R}{v_l(T) - b} + \dots \end{aligned} \quad (33b)$$

Choosing (T, v) as the independent variables, the molar Gibbs-Duhem equation (2.65) becomes

$$\begin{aligned} d\mu &= -s dT + v dP \\ &= -s dT + v \left[\left(\frac{\partial P}{\partial v} \right)_T dv + \left(\frac{\partial P}{\partial T} \right)_v dT \right] \\ &= \left[-s + v \left(\frac{\partial P}{\partial T} \right)_v \right] dT + v \left(\frac{\partial P}{\partial v} \right)_T dv \\ &= T_c \left[-s + \frac{P_c v_c}{T_c} \bar{v} \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{v}} \right] d\bar{T} + P_c v_c \bar{v} \left(\frac{\partial \bar{P}}{\partial \bar{v}} \right)_T d\bar{v} \\ &= R T_c \left\{ \left[-\frac{s}{R} + \frac{3}{8} \bar{v} \left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{v}} \right] d\bar{T} + \frac{3}{8} \bar{v} \left(\frac{\partial \bar{P}}{\partial \bar{v}} \right)_T d\bar{v} \right\} \end{aligned} \quad (34)$$

Now, $\left(\frac{\partial (19)}{\partial \bar{T}} \right)_{\bar{v}}$ gives

$$\left(\frac{\partial \bar{P}}{\partial \bar{T}} \right)_{\bar{v}} = \frac{8}{3\bar{v} - 1} \quad (35)$$

so that, together with (26), we can write (34) as

$$\frac{d\mu}{R T_c} = \left(-\frac{s}{R} + \frac{3\bar{v}}{3\bar{v} - 1} \right) d\bar{T} + 9\bar{v} \left[-\frac{\bar{T}}{(3\bar{v} - 1)^2} + \frac{1}{4\bar{v}^3} \right] d\bar{v} \quad (36)$$

Thus,

$$\begin{aligned} \frac{(d\mu)_{\bar{T}}}{R T_c} &= 9\bar{v} \left[-\frac{\bar{T}}{(3\bar{v} - 1)^2} + \frac{1}{4\bar{v}^3} \right] d\bar{v} \\ \rightarrow \frac{\mu}{R T_c} &= \frac{\bar{T}}{3\bar{v} - 1} - \frac{9}{4\bar{v}} - \bar{T} \ln(3\bar{v} - 1) + C_2(\bar{T}) \end{aligned} \quad (37)$$

where C_2 is an arbitrary function of \bar{T} .

Using

$$\begin{aligned} -\frac{s}{R} + \frac{3\bar{v}}{3\bar{v} - 1} &= -\frac{s_0}{R} - \ln \left[\left(\frac{\bar{T}}{\bar{T}_0} \right)^{3/2} \left(\frac{3\bar{v} - 1}{3\bar{v}_0 - 1} \right) \right] + \frac{3\bar{v}}{3\bar{v} - 1} && \text{[(32) used.]} \\ &= \frac{1}{R T_c} \left(\frac{\partial \mu}{\partial \bar{T}} \right)_{\bar{v}} && \text{[(36) used.]} \end{aligned}$$

$$= \frac{1}{3\bar{v}-1} - \ln(3\bar{v}-1) + \frac{dC_2}{d\bar{T}} \quad [(37) \text{ used.}]$$

we have

$$\frac{dC_2}{d\bar{T}} = \alpha - \ln \bar{T}^{3/2} \quad (38)$$

where

$$\alpha = -\frac{s_0}{R} + \ln[\bar{T}_0^{3/2} (3\bar{v}_0 - 1)] + 1 \quad (38a)$$

Integrating (38) gives

$$\begin{aligned} C_2 &= \alpha \bar{T} + \frac{3}{2} (\bar{T} - \bar{T} \ln \bar{T}) + \text{const} \\ &= \bar{T} \left\{ -\frac{s_0}{R} + \frac{5}{2} - \ln \left[\left(\frac{\bar{T}}{\bar{T}_0} \right)^{3/2} \frac{1}{3\bar{v}_0 - 1} \right] \right\} + \text{const} \end{aligned}$$

so that (37) becomes

$$\begin{aligned} \frac{\mu}{RT_c} &= \frac{\bar{T}}{3\bar{v}-1} - \frac{9}{4\bar{v}} - \bar{T} \left\{ \frac{s_0}{R} - \frac{5}{2} + \ln \left[\left(\frac{\bar{T}}{\bar{T}_0} \right)^{3/2} \left(\frac{3\bar{v}-1}{3\bar{v}_0-1} \right) \right] \right\} + \text{const} \\ &= \frac{\bar{T}}{3\bar{v}-1} - \frac{9}{4\bar{v}} - \bar{T} \ln \left[\left(\frac{\bar{T}}{\bar{T}_0} \right)^{3/2} \left(\frac{3\bar{v}-1}{3\bar{v}_0-1} \right) \right] + \text{const} \end{aligned} \quad (39)$$

where we have used $s_0 = \frac{5}{2}R$. Reverting to the unnormalized variables, we have

$$\frac{\mu}{R} = \frac{bT}{v-b} - \frac{2a}{Rv} - T \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{v-b}{v_0-b} \right) \right] + \text{const} \quad (40)$$

Code

$$\int \frac{1}{3v-1} dv$$

$$\frac{1}{3} \text{Log}[-1+3v]$$

$$9 \int v \left(-\frac{T}{(3v-1)^2} + \frac{1}{4v^3} \right) dv$$

$$9 \left(-\frac{T}{9(1-3v)} - \frac{1}{4v} - \frac{1}{9} T \text{Log}[1-3v] \right)$$

$$\partial_v \left(-\frac{8T}{3(1-3v)} - \frac{6}{v} - \frac{8}{3} T \text{Log}[-1+3v] \right) // \text{Simplify}$$

$$\frac{6}{v^2} - \frac{24Tv}{(1-3v)^2}$$

$$\int \text{Log}[T] dT$$

$$-T + T \text{Log}[T]$$