

**April 11, 2014**  
**DETERMINATION OF THERMODYNAMIC PROPERTIES OF VAPOR USING**  
**VAN DER WAALS' CUBIC EQUATION OF STATE**  
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This appendix considers a restricted case for finding the thermodynamic properties of a substance or mixture of fixed composition with a particular form for its equation of state. The equation of state relates the pressure,  $P$ , to the temperature,  $T$ , and the volume per mole,  $V$ . The independent variables are taken to be  $T$  and  $V$  and the equation of state has the form,

$$P = f(T, V) \quad 1$$

The form for this equation studied here is for a van der Waals cubic equation of state that has the form,

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V^2} \quad 2$$

where  $R$  [= 10.732 psia.-cu.ft./((lb mole)-°R) = 0.7208 atm-ft<sup>3</sup>/((lb mole)-°R)] is the universal gas constant,  $a$  and  $b$  are constants. The usual units for  $a$  are atm-ft<sup>6</sup>/((lb mole)<sup>2</sup>) while for  $b$  they are expressed as ft<sup>3</sup>/((lb mole)). Recall that the corresponding equation of state for an ideal gas is,

$$P = \frac{R \cdot T}{V} \quad 3$$

In this development the fluid vapor is assumed to be adequately represented by Equation 3 for sufficiently low pressures.

The procedure presented here shows that, when  $T$  and  $V$  are specified, (and Equation 2 determines  $P$ ) the values for the entropy,  $S$ , and the enthalpy,  $H$ , may be found. The following development uses Equations 2 and 3 with equations from classical thermodynamics to make possible the determination of the following thermodynamic properties,

$$\begin{aligned} U &= \text{internal energy} \\ S &= \text{entropy} \\ A &= \text{Helmholtz free energy or work function} \\ &= U - T \cdot S \end{aligned} \quad 4$$

$$\begin{aligned} H &= \text{enthalpy} \\ &= U + P \cdot V \\ &= A + T \cdot S + P \cdot V \end{aligned} \quad 5$$

$$\begin{aligned} F &= \text{Gibbs free energy or thermodynamic potential} \\ &= H - T \cdot S \\ &= U + P \cdot V - T \cdot S \end{aligned} \quad 6$$

The first law of thermodynamics for a reversible process is,

$$dU = T \cdot dS - P \cdot dV \quad 7$$

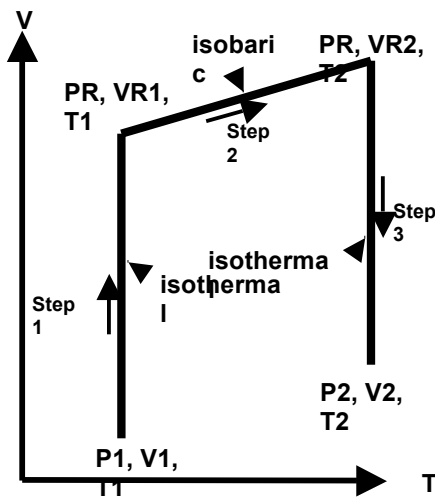
so that, for a reversible process,

$$dA = -P \cdot dV - S \cdot dT \quad 8$$

$$dH = T \cdot dS + V \cdot dP \quad 9$$

$$dF = V \cdot dP - S \cdot dT \quad 10$$

The primary objective here is to enable calculations for changes of  $U$ ,  $A$ ,  $H$  and  $F$  between two states defined by  $P_1, V_1, T_1$  and  $P_2, V_2, T_2$ . The reason for calculating changes is that  $U$ ,  $A$ ,  $H$  and  $F$  all use arbitrary references, like potential energy. A simplification, from a calculation point of view, is to select a  $P, V, T$  path between  $P_1, V_1, T_1$  and  $P_2, V_2, T_2$  that is straightforward to calculate. Any continuous path may be chosen since  $U$ ,  $A$ ,  $H$  and  $F$  are all fluid properties and thus path independent. A specified, reference volume,  $V_{R1}$ , is introduced that is sufficiently large so that for low pressures, in the temperature range for calculation, the ideal gas equation of state, Equation 3, applies. The  $P, V, T$  path used here is in three, reversible process steps as follows,



Step 1:

From  $P_1, V_1, T_1$  along an isothermal path to a volume per mole of  $V_{R1}$ . The end of this step is defined by  $P_R, V_{R1}, T_1$ . Since  $T_1$  and  $V_{R1}$  are known, Equation 3 can be used to find  $P_R$ .

Step 2:

From the end of Step 1,  $P_R, V_{R1}, T_1$ , along a constant pressure path to a temperature of  $T_2$ . The end of this step is defined by  $P_R, V_{R2}, T_2$ . Since  $P_R$  and  $T_2$  are known,  $V_{R2}$  may be found using the ideal gas equation of state, Equation 2 (van der Waals' equation).

Step 3:

From the end of Step 2,  $P_R, V_{R2}, T_2$ , along an isothermal path to a volume per mole of  $V_2$ . The end of this step is defined by  $P_2, V_2, T_2$ .

Step 2 is chosen since the differential changes in enthalpy,  $dH$ , and entropy,  $dS$ , along the constant pressure path for an ideal gas are given by,

$$dH = C_p(T) \cdot dT \quad 11$$

$$dS = \frac{C_p(T)}{T} \cdot dT \quad 12$$

and measured results for  $C_p(T)$  are readily available in the literature (e.g. – Bruce E. Poling, John M. Prausnitz and John P. O'Connell, *The Properties of Gases and Liquids*, Fifth Edition, McGraw-Hill, 2000, Appendix C) in the form,

$$\frac{C_p(T)}{R} = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 + a_4 \cdot T^4 \quad \text{for the vapor state} \quad 13$$

The values given for liquid state are constants,  $C_p^0$ . Consequently, for gases, integration of Equation 11 from  $T_1$  to  $T_2$  gives the enthalpy change,  $\Delta H_2$ , as,

$$H = R \cdot \left[ a_0 \cdot T + \frac{1}{2} \cdot a_1 \cdot T^2 + \frac{1}{3} \cdot a_2 \cdot T^3 + \frac{1}{4} \cdot a_3 \cdot T^4 + \frac{1}{5} \cdot a_4 \cdot T^5 \right] + g(P) \quad 14$$

with  $g(P)$  an arbitrary function of pressure so that,

$$\Delta H_2 = R \cdot \left[ a_0 \cdot (T_2 - T_1) + \frac{1}{2} \cdot a_1 \cdot (T_2^2 - T_1^2) + \frac{1}{3} \cdot a_2 \cdot (T_2^3 - T_1^3) + \frac{1}{4} \cdot a_3 \cdot (T_2^4 - T_1^4) + \frac{1}{5} \cdot a_4 \cdot (T_2^5 - T_1^5) \right] \quad 15$$

and the corresponding entropy change,  $\Delta S_2$ , is obtained by integrating Equation 12,

$$S = R \cdot \left[ a_0 \cdot \ln(T) + a_1 \cdot T + \frac{1}{2} \cdot a_2 \cdot T^2 + \frac{1}{3} \cdot a_3 \cdot T^3 + \frac{1}{4} \cdot a_4 \cdot T^4 \right] + e(P) \quad 16$$

with  $e(P)$  an arbitrary function of pressure so that,

$$\Delta S_2 = R \cdot \left[ a_0 \cdot \ln\left(\frac{T_2}{T_1}\right) + a_1 \cdot (T_2 - T_1) + \frac{1}{2} \cdot a_2 \cdot (T_2^2 - T_1^2) + \frac{1}{3} \cdot a_3 \cdot (T_2^3 - T_1^3) + \frac{1}{4} \cdot a_4 \cdot (T_2^4 - T_1^4) \right] \quad 17$$

For the calculations considered here,  $V_{R1}$ , must be large enough so that only ideal gas vapor properties are used in Step 2.

Step 1 is an isothermal process from  $V_1$  to  $V_{R1}$  so it is best to start by finding the changes of Helmholtz free energy and the entropy. The change in enthalpy is determined from the Helmholtz free energy and entropy. The differential form of the definition for the Helmholtz free energy is,

$$dA = dU - T \cdot dS - S \cdot dT \quad 18$$

This may be combined with the first law of thermodynamics for this reversible process, Equation 7, to eliminate  $dU$  and obtain,

$$dA = -P \cdot dV - S \cdot dT \quad 19$$

As  $A$ ,  $P$ ,  $V$ ,  $S$  and  $T$  are all properties (i.e. – point functions), it follows that,

$$\left. \frac{\partial A}{\partial V} \right|_T = -P \quad 20$$

$$\left. \frac{\partial A}{\partial T} \right|_V = -S \quad 21$$

where the subscript after the vertical line implies that the subscripted variable is held constant during the partial differentiation. Equation 20 may be integrated for the isothermal process. This integration gives the result that the Helmholtz free energy for Step 1 may be expressed as,

$$A = - \int P|_T \cdot dV + h(T) \quad 22$$

where  $h(T)$  is an arbitrary function of temperature and the integral is a function of  $T$  and  $V$ . The corresponding values of entropy for Step 1 may be found using Equation 21 and 22 to obtain,

$$S = \int \left. \frac{\partial P}{\partial T} \right|_T \cdot dV - \frac{dh(T)}{dT} \quad 23$$

and the enthalpy for Step 1 becomes,

$$H = A + T \cdot S + P \cdot V = - \int P|_T \cdot dV + T \cdot \int \left. \frac{\partial P}{\partial T} \right|_T \cdot dV + P \cdot V + h(T) - T \cdot \frac{dh(T)}{dT} \quad 24$$

When the van der Waals equation of state, Equation 2, is substituted into Equations 23 and 24 for Step 1, the result is,

$$S = R \cdot \ln(V - b) - \frac{dh(T)}{dT} \quad 25$$

$$H = R \cdot T \cdot \frac{V}{V - b} - \frac{2 \cdot a}{V} + h(T) - T \cdot \frac{dh(T)}{dT} \quad 26$$

and the corresponding changes for the isothermal process of Step 1,  $\Delta S1$  and  $\Delta H1$ , become.

$$\Delta S1 = R \cdot \ln \left( \frac{V_{R1} - b}{V_1 - b} \right) \quad 27$$

$$\Delta H1 = R \cdot T_1 \cdot \left( \frac{V_{R1}}{V_{R1} - b} - \frac{V_1}{V_1 - b} \right) - 2 \cdot a \cdot \left( \frac{1}{V_{R1}} - \frac{1}{V_1} \right) \quad 28$$

Step 3 is also an isothermal process from  $V_{R2}$  to  $V_2$  so the results for Step 1 may be used to deduce that the changes in entropy and enthalpy,  $\Delta S3$  and  $\Delta H3$ , are,

$$\Delta S_3 = R \cdot \ln \left( \frac{V_2 - b}{V_{R2} - b} \right) \quad 29$$

$$\Delta H_3 = R \cdot T_2 \cdot \left( \frac{V_2}{V_2 - b} - \frac{V_{R2}}{V_{R2} - b} \right) - 2 \cdot a \cdot \left( \frac{1}{V_2} - \frac{1}{V_{R2}} \right) \quad 30$$

In order to complete the definition of S in Equation 25, a reference state must be chosen. In this work the reference state for  $S = S_0$  is temperature  $T_0$  and volume per mole  $V_0$ . The value of  $V_0$  is chosen sufficiently large so that the ideal gas equations are valid. The pressure  $P_0$  at the reference state is found using the equation of state, Equation 4, with  $V = V_0$  and  $T = T_0$ . To find the entropy at any value of temperature,  $T^*$ , volume per mole,  $V^*$ , and pressure,  $P^*$ , that satisfies the equations of state, Equations 2 and 3, a constant pressure change at  $P_0$  is made from  $T_0$  to  $T^*$  and this is followed by an isothermal change at  $T^*$  from  $V_0$  to  $V^*$ . At the end of the constant pressure, ideal gas, process, the volume per mole is  $V_R$  where,

$$V_R = V_0 \cdot \frac{T^*}{T_0} \quad 31$$

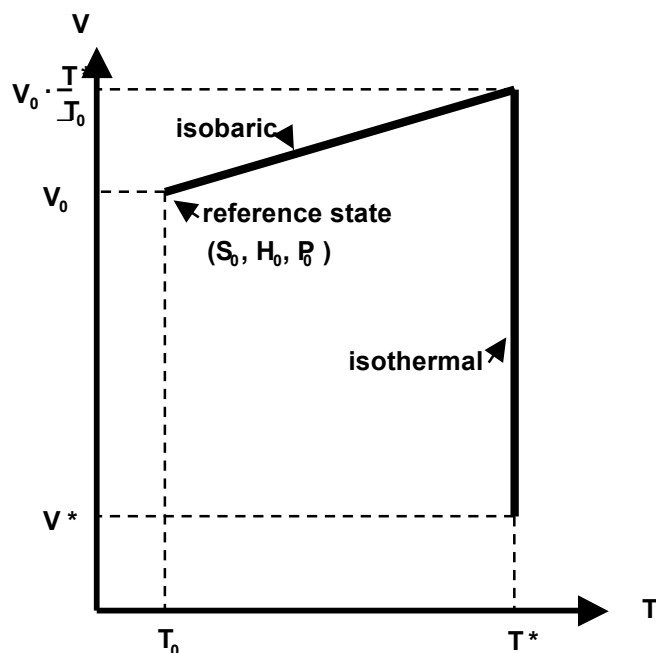
The solutions above are applied to obtain,

$$\begin{aligned} S(T^*, V^*) = & S_0 \\ & + R \cdot \left[ a_0 \cdot \ln \left( \frac{T^*}{T_0} \right) + a_1 \cdot (T^* - T_0) + \frac{1}{2} \cdot a_2 \cdot (T^{*2} - T_0^2) + \frac{1}{3} \cdot a_3 \cdot (T^{*3} - T_0^3) + \frac{1}{4} \cdot a_4 \cdot (T^{*4} - T_0^4) \right] \\ & + R \cdot \ln \left( \frac{V^* - b}{V_R - b} \right) \end{aligned} \quad 32$$

The procedure followed above to determine  $S(T^*, V^*)$  can be followed for the enthalpy. Using the same reference state and setting  $H = H_0$  at the reference state leads to,

$$\begin{aligned} H(T^*, V^*) = & H_0 \\ & + R \cdot \left[ a_0 \cdot (T^* - T_0) + \frac{1}{2} \cdot a_1 \cdot (T^{*2} - T_0^2) + \frac{1}{3} \cdot a_2 \cdot (T^{*3} - T_0^3) + \frac{1}{4} \cdot a_3 \cdot (T^{*4} - T_0^4) + \frac{1}{5} \cdot a_4 \cdot (T^{*5} - T_0^5) \right] \\ & + R \cdot T^* \cdot \left( \frac{V^*}{V^* - b} - \frac{V_R}{V_R - b} \right) - 2 \cdot a \cdot \left( \frac{1}{V^*} - \frac{1}{V_R} \right) \end{aligned} \quad 33$$

The sketch below shows the thermodynamic path followed for Equations 32 and 33. When the formulation of Equations 32 and 33 is used, the change from the reference state to the state in question is found. Obviously, the change between two arbitrary states can be found by applying Equations 33 and 34 to each state and then taking the difference.



When the pressure,  $P$ , the enthalpy,  $H$ , and the entropy,  $S$ , are known for a specified  $T$  and  $V$ , then the other properties follow from,

$U$	= internal energy per mole	$= H - P \cdot V$	34
$A$	= Helmholtz free energy or work function per mole	$= U - T \cdot S$	35
$F$	= Gibbs free energy or thermodynamic potential per mole	$= H - T \cdot S$	36

A typical set of properties is given below for  $\text{CO}_2$ ,

$R$	= $0.7308 \text{ atm-ft}^3/((\text{lb mole})\text{-}^\circ\text{R}) = 10.732 \text{ psia-cu.ft./}((\text{lb mole})\text{-}^\circ\text{R}) = 1.9866 \text{ Btu/}((\text{lb mole})\text{-}^\circ\text{R})$
MW	= 44.01 molecular weight
$a$	= $925.0 \text{ atm-ft}^6/(\text{lb mole})^2 = 7.0184 \text{ psia-ft}^6/\text{lb}^2$
$b$	= $0.686 \text{ ft}^3/(\text{lb-mole}) = 0.015587 \text{ ft}^3/\text{lb}$

For Equation 13,

$a_0$	= 3.259
$a_1$	= $0.7533\text{E-}3 \text{ }^\circ\text{R}^{-1}$
$a_2$	= $0.4636\text{E-}5 \text{ }^\circ\text{R}^{-2}$
$a_3$	= $-0.4071\text{E-}8 \text{ }^\circ\text{R}^{-3}$
$a_4$	= $0.10059\text{E-}11 \text{ }^\circ\text{R}^{-4}$