

We are interested in determining the density reading of the densitometer at the temperature used for the pycnometer reading such that a 1:1 comparison of the two instruments can be made. To do so, we assume the following first order Taylor series:

$$\rho_d(T_p) = \rho_d(T_d) + \frac{\partial \rho_T}{\partial T} \Big|_x (T_p - T_d),$$

where  $\rho_d$  is the density reading of the densitometer,  $T_p$  is the pycnometer temperature reading,  $T_d$  is the densitometer temperature reading, and  $x$  is the mole fraction of ethanol-water. In order to find the partial derivative of density w.r.t temperature, we will first derive a different equation, the partial derivative of true proof TP, and recover the desired derivative from there. First, the density of the fluid with a glass instrument effect  $\rho_T^{AP}$  is (assume density reading by densitometer doesn't have glass instrument effect and is equal to  $\rho_T$ ):

$$\rho_T^{AP} = \rho_T [1 + \alpha(T - T_{60})],$$

where  $\rho_T$  is the density of the fluid without the glass expansion artifact and  $\alpha$  is the thermal expansion coefficient of glass. A general value of  $\alpha$  for glass is  $25 \times 10^{-5} / ^\circ\text{C}$ . Furthermore, we define function  $f$  to convert density readings to apparent proof using Table 6:

$$f: \rho \rightarrow AP.$$

We also define function  $g$  to convert apparent proof and temperature to the true proof using Table 1:

$$g: AP, T \rightarrow TP.$$

All together, we can construct the following relation for determining true proof based on the fluid density at temperature  $T$ :

$$TP = g(f(\rho_T[1 + \alpha(T - T_{60})]), T).$$

Taking the partial derivative of the above TP function yields:

$$\frac{\partial TP}{\partial AP} \Big|_T \frac{\partial f}{\partial \rho} [\partial \rho_T [1 + \alpha(T - T_{60})] + \alpha \rho_T dT] + \frac{\partial g}{\partial T} \Big|_{AP} \partial T = 0.$$

Note that we assume  $x$  and  $TP$  to be constant. Dividing through by  $\partial T$  leads to:

$$\frac{\partial g}{\partial AP} \Big|_T \frac{\partial f}{\partial \rho} \left[ \frac{\partial \rho_T}{\partial T} [1 + \alpha(T - T_{60})] + \alpha \rho_T \right] + \frac{\partial g}{\partial T} \Big|_{AP} = 0.$$

We can now begin rearranging the above equation to solve for the partial derivative of density w.r.t temperature as follows:

$$\left. \frac{\partial g}{\partial AP} \right|_T \frac{\partial f}{\partial \rho} \left[ \frac{\partial \rho_T}{\partial T} [1 + \alpha(T - T_{60})] + \alpha \rho_T \right] = - \left. \frac{\partial g}{\partial T} \right|_{AP}.$$

$$\left[ \frac{\partial \rho_T}{\partial T} [1 + \alpha(T - T_{60})] + \alpha \rho_T \right] = \frac{- \left. \frac{\partial g}{\partial T} \right|_{AP}}{\left. \frac{\partial g}{\partial AP} \right|_T \frac{\partial f}{\partial \rho}} = - \left. \frac{\partial g}{\partial T} \right|_{AP} \frac{\partial AP}{\partial g} \Big|_T \frac{\partial \rho}{\partial f}.$$

Note that we can simplify the partial derivative terms. The cyclic relation is:

$$\left. \frac{\partial g}{\partial T} \right|_{AP} \left. \frac{\partial AP}{\partial g} \right|_T \left. \frac{\partial T}{\partial AP} \right|_g = -1.$$

We can rearrange this to the more useful form (negative sign):

$$\left. \frac{\partial g}{\partial T} \right|_{AP} \left. \frac{\partial AP}{\partial g} \right|_T = - \left. \frac{\partial AP}{\partial T} \right|_g.$$

Applying this relation thus simplifies our expression for the density derivative:

$$\begin{aligned} \frac{\partial \rho_T}{\partial T} &= \frac{- \left. \frac{\partial g}{\partial T} \right|_{AP} \left. \frac{\partial AP}{\partial g} \right|_T \frac{\partial \rho}{\partial f} - \alpha \rho_T}{1 + \alpha(T - T_{60})} \\ &= \frac{\left. \frac{\partial AP}{\partial T} \right|_{TP} \frac{\partial \rho}{\partial AP}}{1 + \alpha(T - T_{60})} - \frac{\alpha \rho_T}{1 + \alpha(T - T_{60})}. \end{aligned}$$

Since we are keeping  $x$  constant, it follows that:

$$\left. \frac{\partial \rho_T}{\partial T} \right|_x = \frac{\left. \frac{\partial AP}{\partial T} \right|_{TP} \left. \frac{\partial \rho}{\partial AP} \right|_x}{1 + \alpha(T - T_{60})} - \frac{\alpha \rho_T}{1 + \alpha(T - T_{60})}.$$

The above equation is appropriate for using densitometer reading  $\rho_T$  at temperature  $T = T_d$ . If the hydrometer (pycnometer) data was used, we would need to substitute  $\rho_T$  with the hydrometer density reading (with instrument effect)  $\rho_T^{AP}$  at  $T = T_p$ :

$$\left. \frac{\partial \rho_T}{\partial T} \right|_x = \frac{\left. \frac{\partial AP}{\partial T} \right|_{TP} \left. \frac{\partial \rho}{\partial AP} \right|_x}{1 + \alpha(T - T_{60})} - \frac{\alpha \rho_T^{AP}}{[1 + \alpha(T - T_{60})]^2}.$$

**Example calculation:** A densitometer reading of 0.8500 g/mL was found for 0.5191 mole fraction ethanol at temperature 31°C. The temperature of the pycnometer reading, for comparison purposes, was 28°C. The relevant terms are, in their algebraic form:

$$x = 0.5191,$$

$$\rho_d(T_d = 31^\circ\text{C}) = 0.8500 \frac{\text{g}}{\text{mL}},$$

$$T_p = 28^\circ\text{C}.$$

Using the true-proof function on fluid true density and temperature of 62°F, the apparent proof of the solution is 168.85°P with an inferred true proof of 159.80°P. We also need to approximate the partial derivatives  $\left. \frac{\partial AP}{\partial T} \right|_{TP}$  and  $\left. \frac{\partial \rho}{\partial AP} \right|_x$ ; however the  $\left. \frac{\partial AP}{\partial T} \right|_{TP}$  is an intractable quantity. Therefore, we revert back to the cyclic relation to determine this quantity.

$$\left. \frac{\partial AP}{\partial T} \right|_{TP} \left. \frac{\partial \rho}{\partial AP} \right|_x = - \left. \frac{\partial TP}{\partial T} \right|_{AP} \left. \frac{\partial AP}{\partial TP} \right|_T \left. \frac{\partial \rho}{\partial AP} \right|_x.$$

The partials are approximated as:

$$\left. \frac{\partial TP}{\partial T} \right|_{AP} \sim \frac{158.8 - 159.1^\circ\text{P}}{31.1111 - 30.5556^\circ\text{C}} = -0.5400 \frac{^\circ\text{P}}{^\circ\text{C}}.$$

$$\left. \frac{\partial AP}{\partial TP} \right|_T \sim \frac{169 - 168^\circ\text{P}}{158.8 - 159.1^\circ\text{P}} = -3.333.$$

$$\left. \frac{\partial \rho}{\partial AP} \right|_x \sim \frac{0.99904 \times (0.86380 - 0.86518) \frac{\text{g}}{\text{mL}}}{160 - 159^\circ\text{P}} = -0.001379 \frac{\text{g}}{\text{mL } ^\circ\text{P}}.$$

The correction for the pycnometer temperature is thus:

$$\begin{aligned} \left. \frac{\partial \rho_T}{\partial T} \right|_x &= \frac{\left. \frac{\partial AP}{\partial T} \right|_{TP} \left. \frac{\partial \rho}{\partial AP} \right|_x}{1 + \alpha(T - T_{60})} - \frac{\alpha \rho_T}{1 + \alpha(T - T_{60})} \\ &= \frac{(0.5400)(3.333)(0.001379) \frac{\text{g}}{\text{mL } ^\circ\text{C}}}{1 + \frac{25 \times 10^{-6}}{^\circ\text{C}}(31 - 15.5556^\circ\text{C})} - \frac{\frac{25 \times 10^{-6}}{^\circ\text{C}} 0.8500 \frac{\text{g}}{\text{mL}}}{1 + \frac{25 \times 10^{-6}}{^\circ\text{C}}(31 - 15.5556^\circ\text{C})} \\ &= 0.002451 \frac{\text{g}}{\text{mL } ^\circ\text{C}} \\ \rho_d(28^\circ\text{C}) &= 0.8500 \frac{\text{g}}{\text{mL}} + 0.002451 \frac{\text{g}}{\text{mL } ^\circ\text{C}} (28 - 31^\circ\text{C}) = \mathbf{0.8426 \frac{g}{mL}} \end{aligned}$$