6.3 Evaluate the difference

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_P - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}}$$

for the ideal and van der Waals gases, and for a gas that obeys the virial equation of state.

6-3

$$d\underline{U} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} dT + \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_T d\underline{V}$$

$$= C_V\, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] d\underline{V}$$ from eq'n 6.2-2.

$$\Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_P = C_V\left(\frac{\partial T}{\partial T}\right)_P + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_P$$

$$\Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_P - C_V = \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_P$$

$$\Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_P - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_P$$

(a) for ideal gas

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = T\left(\frac{\partial \frac{RT}{\underline{V}}}{\partial T}\right)_{\underline{V}} - P$$

$$= \frac{TR}{\underline{V}}\left(\frac{\partial T}{\partial T}\right)_{\underline{V}} - P$$ ($\because \underline{V}$ is constant)

$$= \frac{TR}{\underline{V}} - P = P - P = 0$$

$$\Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_P - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = 0$$

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(b) for van der Waals gases.

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$$

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \frac{RT}{\underline{V}-b} - \left[\frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}\right] = \frac{a}{\underline{V}^2}$$

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2} \Rightarrow \frac{\left(P + \frac{a}{\underline{V}^2}\right)(\underline{V}-b)}{R} = T$$

$$\Rightarrow T = \frac{P\underline{V}}{R} + \frac{a}{R}\underline{V}^{-1} - \frac{Pb}{R} - ab\underline{V}$$

$$\Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial \underline{V}}\right)_P} = \frac{1}{\frac{P}{R} - \frac{a}{R}\underline{V}^{-2} + 0 + 2ab\,\underline{V}^{-3}}$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_{\underline{V}} = \frac{a}{\underline{V}^2} \cdot \frac{1}{\frac{P}{R} - \frac{a}{R\underline{V}^2} + \frac{2ab}{\underline{V}^3}}$$

$$= \frac{a}{\frac{P}{\underline{V}^2 R} - \frac{a}{R} + \frac{2ab}{\underline{V}}}$$

$$= \frac{a\underline{V}^2 R}{P - a\underline{V}^2 + 2abR\underline{V}}$$