Example For Problem 1

Derive an expression for $\frac{\alpha}{k_T}$ where $\alpha = \frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_P$

$k_T = -\frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial P}\right)_T$

Link to complicated problem

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Physical_Chemistry_(Fleming)/04%3A_Putting_the_First_Law_to_Work/4.03%3A_Compressibility_and_Expansivity

Practice problem 1

This problem shows you what steps to take so you can solve the homework problem 1.

Given:

$$\boxed{\frac{\alpha}{k_T} = \left(\frac{\partial P}{\partial T}\right)_V}$$

$$\boxed{PV = nRT}$$

$$\downarrow$$

$$P\bar{V} = RT \qquad \bar{V} = \frac{V}{n}$$

Calculate for ideal gas law:

Start by differentiating ideal gas law with respect to T, holding V constant. This comes from: $\frac{\alpha}{k} = \left(\frac{\partial P}{\partial T}\right)_V$

Dont forget product rule

change of V at constant V is 0

change of T over change of T is 0

$$\underbrace{\bar{V}\left(\frac{\partial P}{\partial T}\right)_V} + \underbrace{\cancel{P\left(\frac{\partial \bar{V}}{\partial T}\right)_V}}_{0} = R\cancel{\left(\frac{\partial T}{\partial T}\right)_V}$$

$$\frac{P\bar{V}}{\bar{V}} = \frac{RT}{\bar{V}} \quad \div T$$

$$\frac{P}{T} = \frac{R}{\bar{V}}$$

$$\frac{\bar{V}\left(\frac{\partial P}{\partial T}\right)_V}{\bar{V}} = \frac{R}{\bar{V}} \qquad = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V}}$$

$$\frac{\alpha}{k_T} = \frac{R}{\bar{V}} = \frac{P}{T}$$

$\alpha = \frac{1}{T}$ $\qquad k = \frac{1}{P}$

Problem 2

a) $C_p = \left(\frac{\partial H}{\partial T}\right)_P$

Differentiate with respect to T, at constant P, bc Cp is constant P, and you have to add T into the mix

$H \equiv U + PV$

show $C_p = \frac{\partial U}{\partial T}\Big)_P + P \frac{\partial V}{\partial T}\Big)_P$

$$\frac{\partial H}{\partial T}\Big)_P = \frac{\partial U}{\partial T}\Big)_P + \cancel{V\left(\frac{\partial P}{\partial T}\right)_P}^{0} + P\left(\frac{\partial V}{\partial T}\right)_P$$

b) $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ using "non-natural derivative" show:

$U = U(T, V)$

$$C_p - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right) + P\left(\frac{\partial V}{\partial T}\right)_P$$

Differentiate with respect to T, at constant P, bc Cp is constant P, and you have to add T into the mix. Why? to get C_V in terms of C_p

$$\frac{dU}{dT}\Big)_P = \frac{\partial U}{\partial T}\Big)_V \cancel{\frac{dT}{dT}\Big)_P} + \frac{\partial U}{\partial V}\Big)_T \frac{dV}{dT}\Big)_P$$

$$C_p = \frac{\partial U}{\partial T}\Big)_P + P\frac{\partial V}{\partial T}\Big)_P$$

$$+P\frac{\partial V}{\partial T}\Big)_P$$

Plug in and cancel stuff at this point

$$C_p - C_V = \underbrace{\left[\frac{dU}{dT}\Big)_P\right] + P\frac{\partial V}{\partial T}\Big)_P}_{C_p} \underbrace{- \frac{\partial U}{\partial T}\Big)_V}_{C_V}$$

$$C_p - C_V = \frac{\partial U}{\partial T}\Big)_V + \frac{\partial U}{\partial V}\Big)_T + \frac{dV}{dT}\Big)_P + P\frac{\partial V}{\partial T}\Big)_P - \frac{\partial U}{\partial T}\Big)_V$$