Answer on Question 50672, Physics, Molecular Physics | Thermodynamics

Question:

Show that the difference of heat capacities for a substance is given by the relation:

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

Answer:

Let us write the formula for the heat capacities at constant pressure and constant volume:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Let's write the entropy as a function of volume V and temperature T:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (1)$$

Then we divide equation (1) by dT at constant pressure and obtain:

$$\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Then we multiply both sides of this equation by T:

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

From the expression for the Helmholtz free energy $F = U - TS$ we have:

$$dF = dU - TdS - SdT = -PdV - SdT$$

Therefore, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and we can rewrite the equation (2):

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \quad (3)$$

Let us consider the equation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$. We multiply the left-hand side of the equation by $\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$ and the rigth-hand side of one by (-1):

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

Therefore, $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$ (4).

So, we substitute equation (4) into equation (3) and obtain:

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$