$\boxed{3.7}$ Prove: $C_p - C_v = \dfrac{-k\left[\frac{\partial}{\partial T}\left(T\left(\frac{\partial \ln Q}{\partial V}\right)_T\right)\right]_V^2}{\left(\frac{\partial^2 \ln Q}{\partial V^2}\right)_T} \geq 0$

Holding N constant, we can use 1.4.17 and 1.4.18: $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$, $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\Big|_V + \frac{\partial S}{\partial V}\Big|_T \cdot \frac{\partial V}{\partial T}\Big|_P\right) \text{ by } \overset{\text{Appendix}}{\text{H.1d}}$$

$$= C_V + T\frac{\partial S}{\partial V}\Big|_T \cdot \frac{\partial V}{\partial T}\Big|_P \implies \underline{C_P - C_V = T\frac{\partial S}{\partial V}\Big|_T \cdot \frac{\partial V}{\partial T}\Big|_P}$$

(Now, by H.1c, $-1 = \frac{\partial V}{\partial T}\Big|_P \frac{\partial T}{\partial P}\Big|_V \frac{\partial P}{\partial V}\Big|_T \implies \frac{\partial V}{\partial T}\Big|_P = \dfrac{-1}{\frac{\partial T}{\partial P}\Big|_V \frac{\partial P}{\partial V}\Big|_T}$)

$$\therefore C_P - C_V = \frac{-T\frac{\partial S}{\partial V}\Big|_T}{\frac{\partial T}{\partial P}\Big|_V \frac{\partial P}{\partial V}\Big|_T}$$

(Further, by H.1a, $\dfrac{\frac{\partial S}{\partial V}\Big|_T}{\frac{\partial T}{\partial P}\Big|_V} = \frac{\partial S}{\partial V}\Big|_T \frac{\partial P}{\partial T}\Big|_V \overset{\text{by H.7a}}{=} \frac{\partial P}{\partial T}\Big|_V \frac{\partial P}{\partial T}\Big|_V = \left(\frac{\partial P}{\partial T}\Big|_V\right)^2$)

$$\text{☆} \quad \therefore C_P - C_V = \frac{-T\left(\frac{\partial P}{\partial T}\Big|_V\right)^2}{\frac{\partial P}{\partial V}\Big|_T} \geq 0$$

(b/c $-T\left(\frac{\partial P}{\partial T}\Big|_V\right)^2$ is clearly ≤ 0, and The denominator must be negative b/c if pressure grows with volume, we have a very bad situation!)

Now, $A = -kT\ln Q$, and by H.6c, $P = -\left(\frac{\partial A}{\partial V}\right)\Big|_T = kT\frac{\partial \ln Q}{\partial V}\Big|_T$ ⊕

So, take a derivative: $\left(\frac{\partial P}{\partial V}\right)_T = kT\frac{\partial^2 \ln Q}{\partial V}\Big|_T$

and another: $\left(\frac{\partial P}{\partial T}\right)_V = k\left(\frac{\partial}{\partial T}\left(T \cdot \frac{\partial \ln Q}{\partial V}\Big|_T\right)\right)_V$

Plug these into ☆:

$$\boxed{C_P - C_V = \frac{-k\left[\frac{\partial}{\partial T}\left(T \cdot \frac{\partial \ln Q}{\partial V}\Big|_T\right)\right]_V^2}{\frac{\partial^2 \ln Q}{\partial V^2}\Big|_T} \geq 0} \quad \square$$

Now, let's verify that $C_P - C_V = Nk$ for an ideal gas.

$P = kT\frac{\partial \ln Q}{\partial V}\Big|_T$ from ⊕, and for an ideal gas $P = \frac{NkT}{V} \implies \frac{N}{V} = \frac{\partial \ln Q}{\partial V}$

$\implies$ The Numerator becomes $-k\left(\frac{N}{V}\right)^2$

$\implies$ The Denominator becomes $\frac{\partial^2 \ln Q}{\partial V^2} = \frac{\partial}{\partial V}\frac{N}{V} = \frac{-N}{V^2}$

$\therefore C_P - C_V = \dfrac{-k\left(\frac{N}{V}\right)^2}{\frac{-N}{V^2}} = \boxed{kN}$.

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