A Thermodynamic Dilemma

look ahead- ΔS for changes in T,P; (always $\Delta S = \int_{initial}^{final} \frac{đq_{rev}}{T}$)

$S(T,P)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{n\bar{C}_P}{T} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$S(T,V)$:

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

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\bar{C}_v}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

ideal gas

$$\Delta S = n\bar{C}_P \ln\left(\frac{T_{final}}{T_{initial}}\right) - nR \ln\left(\frac{P_{final}}{P_{initial}}\right)$$ E&R eqn 5.19

$$\Delta S = n\bar{C}_v \ln\left(\frac{T_{final}}{T_{initial}}\right) + nR \ln\left(\frac{V_{final}}{V_{initial}}\right)$$ E&R eqn 5.18

the problem

isothermal double volume HW#5, prob.26

$n=1,\ T=T,\ V=V_1,\ P=P_1$ ⇨ $n=1,\ T=T,\ V=2V_1,\ P=\frac{1}{2}P_1$

$\Delta S > 0$

Prof says:

$$\Delta S = n\bar{C}_v \ ln\left(\frac{T_{final}}{T_{initial}}\right) + nR\ ln\left(\frac{V_{final}}{V_{initial}}\right)$$ *E&R eqn 5.18*

$$\Delta S = \bar{C}_v \ ln\left(\frac{T}{T}\right) + R\ ln\left(\frac{2V}{V}\right)$$

⇩

$\Delta S = R \ln(2)$

the dilemma

but really good student asks:
don't we have to take into account both

$$\left(\frac{\partial S}{\partial V}\right)_T \; and \; \left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V} \quad from\ S(T,V)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P} \quad from\ S(T,P)$$

$$\Delta S_{P\ change} = -\,nR\ ln\left(\frac{P_{final}}{P_{initial}}\right) = -R\ln\left(\frac{1}{2}\right) = R\ln 2$$

$$\Delta S_{V\ change} = \ nR\ ln\left(\frac{V_{final}}{V_{initial}}\right) = R\ln 2$$

$$\Delta S_{total} = 2R\ln 2$$

a little funky extracting from BOTH S(T,V) and S(T,P) to calculate in terms of a P and V change

what we really need to do to calculate ΔS in terms of both a P and V change

$$S(P,V):$$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

know that

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{n\bar{C}_P}{T} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\bar{C}_V}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

can YOU evaluate

$$\left(\frac{\partial S}{\partial V}\right)_P = ?$$

and

$$\left(\frac{\partial S}{\partial P}\right)_V = ?$$

in terms of $\bar{C}_V, \bar{C}_P, P, V, T$

and their derivatives?

evaluate

$$\left(\frac{\partial S}{\partial V}\right)_P = ?$$

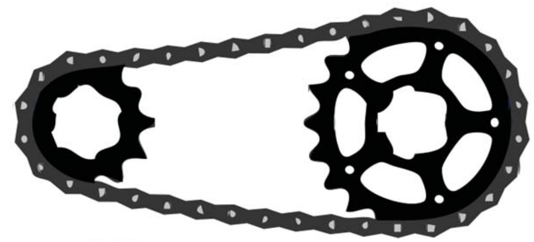
and

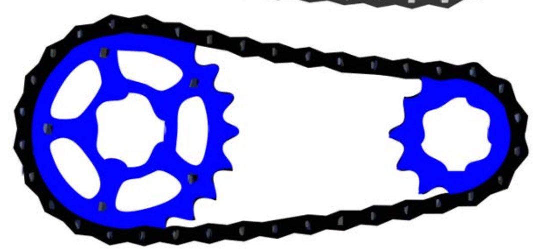
$$\left(\frac{\partial S}{\partial P}\right)_V = ?$$

in terms of $\bar{C}_V, \bar{C}_P, P, V, T$

and their derivatives

HINT





CHAIN RULE

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

and

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

CHAIN RULE

evaluate for ideal gas

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{n\bar{C}_p}{T}\frac{P}{nR} = \bar{C}_p \frac{P}{RT} = \frac{n\bar{C}_p}{V}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \frac{n\bar{C}_V}{T}\frac{V}{nR} = \bar{C}_V \frac{V}{RT} = \frac{n\bar{C}_V}{P}$$

IS NOW in terms of $\bar{C}_V, \bar{C}_P, P, V, T$

and their derivatives

what we really need to do to calculate ΔS in terms of both a P and V change

$$S(P,V):$$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$dS = \frac{n\bar{C}_V}{P} dP + \frac{n\bar{C}_P}{V} dV$$

$$\Delta S = n\bar{C}_V \ln\left(\frac{P_f}{P_i}\right) + n\bar{C}_P \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = \bar{C}_V \ln\left(\frac{\frac{1}{2}P}{P}\right) + \bar{C}_P \ln\left(\frac{2V}{V}\right)$$

$$\Delta S = -\bar{C}_V \ln 2 + \bar{C}_P \ln 2$$

$$\Delta S = (\bar{C}_P - \bar{C}_V)\ln 2$$

what is $(\bar{C}_P - \bar{C}_V)$ *for ideal gas ?*

and the coup de grace

$$\Delta S = (\bar{C}_P - \bar{C}_V)\ln 2$$

$$what\ is\ (\bar{C}_P - \bar{C}_V)\ for\ ideal\ gas\ ?$$

$$(\bar{C}_P - \bar{C}_V) = R\ \ for\ ideal\ gas$$

$$\Delta S = (\bar{C}_P - \bar{C}_V)\ ln2$$

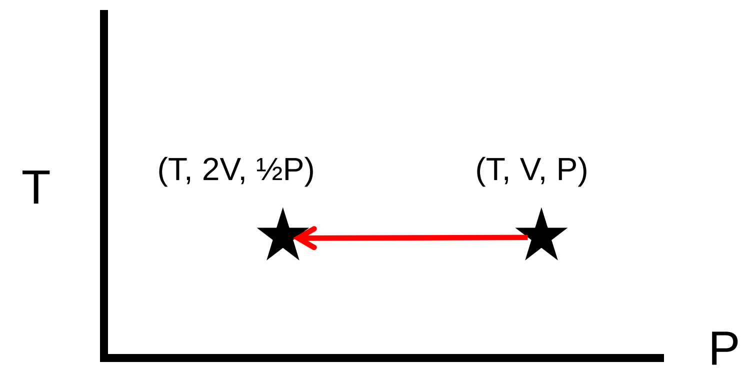
$$\Delta S = R\ ln2$$

moral of the story (T,V,P) → (T,2V,½P) $\Delta S = nR\ \ln 2$

$S(T,P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\Delta S = n\bar{C}_P \ln\left(\frac{T_{final}}{T_{initial}}\right) - nR\ln\left(\frac{P_{final}}{P_{initial}}\right) \quad \textit{ideal gas}$$



$S(T,V)$

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

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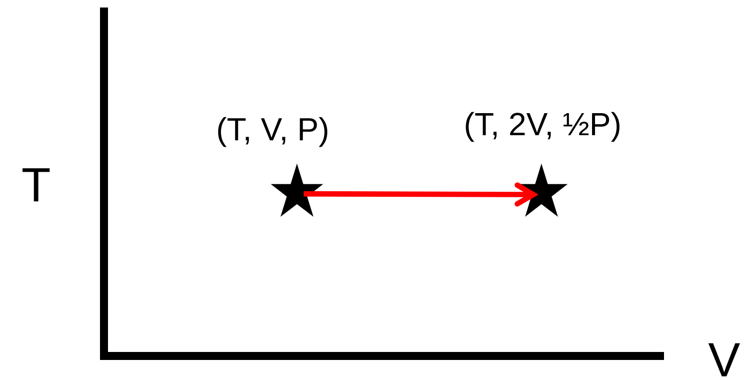

$S(P,V)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$\Delta S = n\bar{C}_V \ln\left(\frac{P_f}{P_i}\right) + n\bar{C}_P \ln\left(\frac{V_f}{V_i}\right) \quad \textit{ideal gas}$$