

Thermodynamics – Solution, Th. 5

As a guide to completing your self-assessment, please use the following correspondence: Unsuccessful: (0 – 3 marks out of 10); Partially Successful: (4 – 7 marks out of 10); Successful (8 – 10 marks out of 10). Please also give information on any parts which you found difficult, as this will allow me to go over any common issues in the workshops. You can also talk individually to myself, and other staff members at these about any issues you faced when solving the problem.

The following Maxwell Relation may be useful when solving this problem. It is derived by considering the Gibbs function, $G = U + pV - TS$,

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

Consider the entropy as a function of temperature and pressure, $S = S(p, T)$.

First, derive the second TdS equation given below,

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp.$$

We are told that $S = S(T, p)$, so writing its total derivative and multiplying through by **T**

$$TdS = T \left(\frac{\partial S}{\partial T}\right)_p dT + T \left(\frac{\partial S}{\partial p}\right)_T dp \quad [1 \text{ mark}]$$

Heat capacity is related to the gradient of entropy with temperature, so $C_p = T \left(\frac{\partial S}{\partial T}\right)_p$ by definition, which takes care of the first term. Using the Maxwell relation given in the question on the second term gives the result,

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp$$

[2 marks – only award 2 if all subscripts of what is held constant correct and present!]

Hence show that in an isothermal process, at T_0 , the heat change can be related to the isobaric expansivity $\beta_p = 1/V \left(\frac{\partial V}{\partial T}\right)_p$, via the following relationship

$$\delta Q = -T_0 \beta_p V dp.$$

If ten moles of water, at 1.0°C , and occupy a volume of $1.8 \times 10^{-4} \text{ m}^3$ and have a volume expansivity coefficient $\beta_p = -50 \times 10^{-6} \text{ K}^{-1}$, what is the heat transferred to the water, if the pressure is increased from 1.0 to 10 atm isothermally?

[Hint: Can you take the liquid to be incompressible here? Why?]

At constant temperature, $dT = 0$ and we know by definition that $TdS = \delta Q$ for a reversible process, hence we have that

$$\delta Q = TdS = 0 - T \left(\frac{\partial V}{\partial T}\right)_p dp.$$

But, using the definition of the volume expansivity, we have $V\beta_p = \left(\frac{\partial V}{\partial T}\right)_p$, so this becomes

$$\delta Q = -T\beta_p V dp. \quad [1 \text{ mark}]$$

The total heat change with pressure from A to B is obtained by integrating the above between the two states. As we are dealing with liquid water, the volume as the pressure increases can be taken as constant $\sim V_0$, since liquids are approximately incompressible.

$$\Delta Q_{AB} = \int_A^B -T\beta_p V dp \approx -T_0 V_0 \beta_p \int_{1\text{atm}}^{10\text{atm}} dp \quad [1 \text{ mark}]$$

$$\therefore \Delta Q_{AB} \approx -T_0 V_0 \beta_p [p]_1^{10}$$

$$= -274 \text{ K} \times 1.8 \times 10^{-4} \text{ m}^3 \times -50 \times 10^{-6} \text{ K}^{-1} \times (10 - 1) \text{ atm} = 2.2 \text{ J}. \quad [1 \text{ mark}]$$

Derive the general relation given below, and evaluate the expression for one mole of monoatomic ideal gas, for which $\gamma = 5/3$,

$$C_p = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_s.$$

[Hint: recall that the equation of state for an adiabatic process for an ideal gas is pV^γ .]

By definition, $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$. Applying the reciprocity theorem to this (cyclic relation)

$$C_p = -T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_s.$$

Using the Maxwell relation given in the question, $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$, leads to the result

$$C_p = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_s. \quad [1 \text{ mark}]$$

For an ideal gas $V = RT/p_0$ at constant pressure, and in a constant entropy process, $pV^\gamma = \text{const}$, or (using the ideal gas law) $p^{1-\gamma} T^\gamma = \text{const}/R$. Calculating the partial derivatives,

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p},$$

$$(1 - \gamma) p^{-\gamma} \left(\frac{\partial p}{\partial T} \right)_s = \frac{\text{const}}{R} \left(-\frac{\gamma}{T^{\gamma-1}} \right) \Rightarrow \left(\frac{\partial p}{\partial T} \right)_s = \left(\frac{\gamma}{\gamma - 1} \right) \frac{\text{const}}{R p^\gamma T^{\gamma-1}}$$

The constant, from $p^{1-\gamma} T^\gamma = \text{const}/R$, can be substituted back in

$$= \left(\frac{\gamma}{\gamma - 1} \right) \frac{p^{1-\gamma} T^\gamma}{R p^\gamma T^{\gamma-1}} = \left(\frac{\gamma}{\gamma - 1} \right) \frac{p}{T}. \quad [2 \text{ marks}]$$

$$C_p = -T \frac{R}{p} \left(\frac{\gamma}{\gamma - 1} \right) \frac{p}{T} = \left(\frac{\gamma}{\gamma - 1} \right) R.$$

Now, for an monoatomic ideal gas, $\gamma = 5/3$, and so we find

$$C_p = \frac{5/3}{2/3} R = \frac{5}{2} R.$$

This is as we expect from Level 1!

[1 mark]