

Thermodynamics – Solution, Th. 2

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.

- a) A volume of ideal gas is initially confined to one half of a container by a partition. Experiments show that when the partition is removed, thereby allowing the gas to expand freely to fill the total volume of the cylinder, the temperature of the gas doesn't change. Use the concept of differentials to show that the *internal energy* of an ideal gas can only depend upon its temperature and not its volume or pressure i.e., $U = U(T)$.
 [Hint: When the partition is removed, the gas expands freely. As a consequence, no heat is required to be input to accomplish this. Similarly, as the expansion is a free expansion, no work is done either by or on the gas.]

In a free expansion no work is done, $\delta W = 0$ and no heat is input, $\delta Q = 0$. Hence from the first law, there cannot be any internal energy change, $dU = \delta Q + \delta W = 0$. [1 mark]

Since the internal energy is a function of state it can be written as a function of (any) two (independent) variables – thermodynamic coordinates. First, considering $U = U(V, T)$, its total differential is

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT.$$

[1 mark]

The experiments tell us that $dT = 0$, (no temperature change) and we know that in a free expansion $dU = 0$, so we find $0 = \left(\frac{\partial U}{\partial V}\right)_T dV$. As $dV \neq 0$ (a volume change must happen during the expansion, but without any work being done), we must have that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and the internal energy cannot depend on volume, i.e. $U \neq U(V)$. [1 mark]

If instead, the internal energy is a function of pressure and temperature, $U = U(p, T)$,

$$dU = \left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT,$$

using a similar argument to above shows we must have $\left(\frac{\partial U}{\partial p}\right)_T dp = 0$. As $dp \neq 0$ (a pressure decrease accompanies a volume change if the temperature is constant), we have $\left(\frac{\partial U}{\partial p}\right)_T = 0$ so U cannot depend on pressure. Thus, the only logical explanation is that the internal energy depends on temperature only, i.e. $U = U(T)$. [1 mark]

- b) One mole of an ideal gas changes adiabatically from the state described by (p_i, V_i, T_i) to the state (p_f, V_f, T_f) . Calculate the sign and magnitude of the process work via an explicit integration in the case that the final volume is less than the initial volume $V_f < V_i$, i.e. calculate

$$W_{i \rightarrow f} = \int_{V_i}^{V_f} \delta W.$$

The equation of state for an ideal gas in an adiabatic process is $pV^\gamma = \text{const}$, which we denote by k . The differential form of work for a gas is given by $\delta W = -pdV$. [1 mark]

We can thus calculate the work as

$$W_{i \rightarrow f} = \Delta W = - \int_i^f p dV = -k \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = \frac{-k}{(1-\gamma)} [V^{1-\gamma}]_{V_i}^{V_f} \equiv + \frac{k}{(\gamma-1)} [V_f^{1-\gamma} - V_i^{1-\gamma}].$$

[1 mark]

This can be written as

$$W_{i \rightarrow f} = \frac{k}{\gamma-1} V_f^{1-\gamma} \left(1 - \left(\frac{V_i}{V_f} \right)^{1-\gamma} \right) \equiv \frac{k}{\gamma-1} V_f^{1-\gamma} \left(1 - \left(\frac{V_f}{V_i} \right)^{\gamma-1} \right).$$

Since k and V_f are both positive and $\gamma > 1$ always ($\gamma = C_p/C_V$ and $C_p > C_V$) the terms before the bracket are all positive. Therefore, the sign of the work depends upon whether $\left(V_f/V_i \right)^{\gamma-1}$ is greater or less than 1. In a compression this ratio is less than one, and it is raised to a positive power. The work is thus positive in line with our expectations (work done on a gas, closing a piston in a compression is always positive). [1 mark]

- c) During a recent exhibition of historic manuscripts at Open Treasure in Durham Cathedral, one such item is found to be giving off an exotic form of gas. Preliminary experiments in Durham have shown that the equation of state is possibly given by

$$p = aT \ln V + \frac{bT}{V},$$

where a and b are constants of appropriate dimensions. Calculate the work done in compressing a sample of this gas, isothermally at a temperature T_0 , to one hundredth of its original volume so that it can be sent away to the National Physical Laboratory for further analysis.

The differential work done is, as always, $\delta W = -pdV$, so we get the total work by integrating at constant temperature, T_0 with $V_0 \rightarrow V_0/100$.

$$\Delta W_{1 \rightarrow 2} = \int_{V_0}^{\frac{V_0}{100}} -pdV = - \int_{V_0}^{\frac{V_0}{100}} \left(aT_0 \ln V + \frac{bT_0}{V} \right) dV = -aT_0 \int_{V_0}^{\frac{V_0}{100}} \ln V dV + bT_0 \int_{V_0}^{\frac{V_0}{100}} \frac{dV}{V}.$$

[1 mark]

$$\begin{aligned} \Delta W_{1 \rightarrow 2} &= -aT_0 [V \ln V - V]_{V_0}^{V_0/100} - bT_0 [\ln V]_{V_0}^{V_0/100} \\ &= -aT_0 \left[\frac{V_0}{100} \ln \left(\frac{V_0}{100} \right) - \frac{V_0}{100} - V_0 \ln V_0 + V_0 \right] - bT_0 \left[\ln \left(\frac{V_0}{100} \right) - \ln V_0 \right] \\ &= -\frac{aT_0 V_0}{100} [99 - \ln(100V_0^{99})] + bT_0 \ln 100. \end{aligned}$$

[2 marks]