

## Thermodynamics – Solution, Th. 1

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) The first part of the problem gives you chance to look at the properties of functions which may be either exact or inexact differentials.
- i) A gas has equation of state given by

$$pV = RT + \frac{aT^2}{V},$$

where  $a$  is some constant. Determine the total derivative of the pressure,  $dp$ .

The total differential of the function  $p = p(V, T)$  is given by

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

[1 mark]

Now  $p = \frac{RT}{V} + \frac{aT^2}{V^2}$ , so  $\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2aT^2}{V^3}$  and  $\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} + \frac{2aT}{V^2}$  so

$$dp = -\left(\frac{RT}{V^2} + \frac{2aT^2}{V^3}\right)dV + \left(\frac{R}{V} + \frac{2aT}{V^2}\right)dT.$$

[1 mark]

- ii) Show that the following function is in fact exact,
- $$z = x^9y^3 + 5x^{-3}y^4.$$

In a similar way to above, the total differential is given by

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = (9x^8y^3 - 15x^{-4}y^4)dx + (3x^9y^2 + 20x^{-3}y^3)dy.$$

Using the definition for differentials, and taking  $M(x, y) = \left(\frac{\partial z}{\partial x}\right)_y$  and  $N(x, y) = \left(\frac{\partial z}{\partial y}\right)_x$ ,

the test which must be satisfied for exactness is  $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ . [1 mark]

Computing these derivatives, we find

$$\left(\frac{\partial M}{\partial y}\right)_x = 27x^8y^2 - 60x^{-4}y^3 \text{ and } \left(\frac{\partial N}{\partial x}\right)_y = 27x^8y^2 - 60x^{-4}y^3.$$

These are identical, so the differential is exact.

[1 mark]

- iii) Determine whether the differentials given below are exact or inexact.

$$da = \frac{4}{3}b^3 \exp(5c) db + \frac{5b^4}{3} \exp(5c) dc ; \quad dI = 12p^2T \sin T dp - 4p^3T \cos T dT.$$

Considering the function  $da$ ,  $M(b, c) = \left(\frac{\partial a}{\partial b}\right)_c = \frac{4}{3}b^3 \exp(5c)$  and  $N(b, c) = \left(\frac{\partial a}{\partial c}\right)_b =$

$\frac{5b^4}{3} \exp(5c)$ . Differentiating with respect to the other variable

$$\left(\frac{\partial M}{\partial c}\right)_b = \frac{20b^3}{3} \exp(5c) \quad ; \quad \left(\frac{\partial N}{\partial b}\right)_c = \frac{20b^3}{3} \exp(5c).$$

These are identical so this is an exact differential.

[1 mark]

Considering the functions  $M(p, T) = \left(\frac{\partial I}{\partial p}\right)_T = 12p^2 T \sin T$  and  $N(p, T) = \left(\frac{\partial I}{\partial T}\right)_p = -4p^3 T \cos T$ , differentiation with respect to the other variable gives,

$$\left(\frac{\partial M}{\partial T}\right)_p = 12p^2(\sin T + T \cos T) \quad ; \quad \left(\frac{\partial N}{\partial p}\right)_T = -12p^2 T \cos T.$$

These are not identical so the function is inexact.

[1 mark]

- b) Two bodies having temperature independent heat capacities  $C_1$  and  $C_2$  are initially at temperatures  $T_1$  and  $T_2$ . They are brought into contact through a diathermal wall and allowed to reach an equilibrium state.

- i) Show that the final temperature is in general given by

$$T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}.$$

Block 1 undergoes a temperature change  $T_1 \rightarrow T_f$ , and similarly  $T_2 \rightarrow T_f$  for block 2. The energies supplied (removed) from the blocks are  $\Delta Q_{1f} = \int C_1 dT = C_1(T_f - T_1)$  and  $\Delta Q_{2f} = C_2(T_f - T_2)$ . One of the blocks undergoes a temperature rise, the other a temperature fall. Thus, one block loses energy and the other gains an equivalent amount, so  $\Delta Q_{1f} = -\Delta Q_{2f}$ , always. It doesn't matter which block starts off hottest. Therefore

$$C_1(T_f - T_1) = C_2(T_2 - T_f) \quad ; \quad T_f(C_1 + C_2) = C_1 T_1 + C_2 T_2 \quad \Rightarrow \quad T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}.$$

[1 mark]

- ii) If  $C_1 \gg C_2$ , show that the final temperature can be approximated by

$$T_f \approx T_1 + \frac{C_2}{C_1}(T_2 - T_1).$$

The result from the last section can be written as

$$T_f = \frac{C_1 \left(T_1 + \frac{C_2}{C_1} T_2\right)}{C_1 \left(1 + \frac{C_2}{C_1}\right)} = \frac{\left(T_1 + \frac{C_2}{C_1} T_2\right)}{\left(1 + \frac{C_2}{C_1}\right)}.$$

Expand the denominator in a Binomial series,  $(1 + x)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 \dots, |x| < 1$ .

$$T_f = \left(T_1 + \frac{C_2}{C_1} T_2\right) \left(1 - \frac{C_2}{C_1} + \left(\frac{C_2}{C_1}\right)^2 + \dots\right) = T_1 - \frac{C_2}{C_1} T_1 + \frac{C_2}{C_1} T_2 + O\left(\frac{C_2}{C_1}\right)^2$$

$$T_f \approx T_1 + \frac{C_2}{C_1}(T_2 - T_1).$$

[2 marks]

Hence explain why the material of heat capacity  $C_2$  would be appropriate to use to make a thermometer.

If the thermometer is initially at  $T_2$ , the final temperature of the combined thermometer and body remains (very) close to the body's original temperature,  $T_1$ . In other words, the presence of the thermometer doesn't really affect the measurement.

[1 mark]