

**THERMODYNAMICS: Examples Sheet 1**

*Most of the questions on this course have a descriptive part which is best answered as 'brief notes'. It is important that you think carefully about these parts of the questions as this will help you understand the concepts involved and give you a starting point for discussion with your supervisor. There are two question sheets for this course – this one covers the first 8 lectures*

**1. First Law; heat capacities**

An isolated vessel of fixed volume  $V_0$  contains a mixture of 1 mol of  $H_2$ , 0.5 mol of  $O_2$  and 2 mol of  $N_2$  at pressure  $p_0 = 1\text{ atm} = 10^5\text{ Pa}$  and temperature 300K. The gas is then ignited by a spark of negligible energy. It is found that  $2.8 \times 10^5\text{ J}$  of heat can be extracted in returning the system to its original temperature. Assume that  $C_V$  is constant and takes values  $26.4\text{ J mol}^{-1}\text{ K}^{-1}$  for  $N_2$  and  $39.1\text{ J mol}^{-1}\text{ K}^{-1}$  for water vapour. For simplicity assume that the water vapour does not condense.

- (a) What is the final pressure?
- (b) Use the First Law to estimate the maximum temperature and pressure reached by the gases left after ignition.
- (c) Estimate the temperature of a flame formed by burning the same mixture of gases at atmospheric pressure. Why is it lower than in (b)? [Note that  $C_p$  rather than  $C_V$  is needed for this part.]

**2. A couple of typical section A questions**

A cubic metre of air at  $0^\circ\text{ C}$  and 1 atm is compressed reversibly to 10 atm.

- (a) What is the final temperature if it is compressed adiabatically?
- (b) How much heat must be removed if it is compressed isothermally?

**3. The First Law and expansion of an ideal gas**

Two thermally isolated cylinders, A and B, of equal volume, both equipped with pistons, are connected by a valve. Initially A has its piston fully withdrawn and contains a monatomic gas at temperature  $T_0$ , while B has its piston fully inserted and the valve is closed. Calculate the final gas temperature in each cylinder after the following operations, each of which starts with the same initial configuration. Assume the thermal capacity of the cylinders is negligible. (continued overleaf)

- (a) The valve is fully opened and the gas is slowly drawn into B by pulling out piston B; piston A remains stationary.
- (b) Piston B is fully withdrawn and the valve opened slightly. The gas is then driven as far as it will go by pushing in piston A at such a rate that the pressure in A remains constant; the cylinders are in thermal contact.
- (c) As in (b), but the cylinders are thermally isolated from each other.
- (d) Piston B is fully withdrawn and the valve is then opened; the cylinders are in thermal contact.
- (e) As in (d), but the cylinders are thermally isolated from each other.

*[Hint – you may find it useful to consider conservation of energy, and the constancy of the total number of mol of gas present. In (c) and (e) you should also consider what kind of change was undergone by that part of the gas which finally remains in A.]*

#### 4. The Second Law

- (a) Prove that Clausius' statement of the Second Law of Thermodynamics follows from Kelvin's statement, and vice versa.
- (b) The  $p$ - $V$  diagram for a fluid contains a family of adiabatic curves. By constructing a suitable three-sided cycle containing one isothermal curve, prove that no two adiabatic curves can intersect.

#### 5. Heat engines

What is a Carnot Cycle? How may it be used to define an absolute thermodynamic scale of temperature?

In a Stirling heat engine, a working substance, which may be assumed to be an ideal monatomic gas, at initial volume  $V_1$  and temperature  $T_1$ , takes in heat at constant volume until its temperature is  $T_2$ , and then expands isothermally until its volume is  $V_2$ . It gives out heat at constant volume until its temperature is again  $T_1$  and then returns to its initial state by isothermal contraction. Show that the efficiency  $\varepsilon$  is given by:

$$\frac{1}{\varepsilon} = \frac{T_2}{T_2 - T_1} + \frac{3}{2 \ln(V_2/V_1)}.$$

Compare with a Carnot engine operating between the same two temperatures.

## 6. A couple of Section A questions

- (a) A freezer unit has a 1 kW compressor, and can maintain the refrigerated space at  $-10^{\circ}\text{C}$  while the ambient temperature is  $20^{\circ}\text{C}$ . It is claimed that the unit has a refrigeration capacity of 2 kW. Is this claim consistent with the laws of thermodynamics?
- (b) A heat pump maintains the temperature of a house at  $20^{\circ}\text{C}$  using heat from the air outside. Estimate the factor by which the power consumption rises when the outside temperature falls from  $10^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .

## 7. Entropy changes

Calculate the change in entropy of the Universe as a result of each of the following operations:

- (a) A copper block of mass 0.4 kg and thermal capacity  $150 \text{ J K}^{-1}$  at  $100^{\circ}\text{C}$  is placed in a lake at  $10^{\circ}\text{C}$ .
- (b) The same block at  $10^{\circ}\text{C}$  is dropped from a height of 100 m into the lake.
- (c) Two such blocks, at  $100^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ , are joined together.
- (d) A  $1 \mu\text{F}$  capacitor is connected to a 100 V reversible battery at  $0^{\circ}\text{C}$ .
- (e) A  $1 \mu\text{F}$  capacitor, after charging to 100 V, is discharged through a resistor at  $0^{\circ}\text{C}$ .
- (f) One mol of ideal gas at  $0^{\circ}\text{C}$  is expanded reversibly and isothermally to twice its initial volume.
- (g) The same expansion as in (f) is carried out reversibly and adiabatically.
- (h) The same expansion as in (f) is carried out by opening a valve to an evacuated container of equal volume.

## 8. Heat engines and Entropy

Three identical bodies of constant heat capacity are initially at temperatures 300, 300 and 100 K. If no heat or work is supplied from outside, what is the highest temperature to which any of the bodies can be raised by the operation of heat engines? [*Hint - think about the changes of energy and entropy.*]

## 9. Analytical Thermodynamics

(a) Show that for a gas (or any  $P$  -  $V$  system):

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - P$$

(b) In a Joule expansion there is no change in internal energy. The temperature change is given by the Joule coefficient  $\left(\frac{\partial T}{\partial V}\right)_U$ . Show that:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left( T \left(\frac{\partial p}{\partial T}\right)_V - P \right).$$

Evaluate the Joule coefficient for the case of a van der Waals gas for which the equation of state (for 1mol of gas) is  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ . Why would you normally expect this to be negative for real gases?

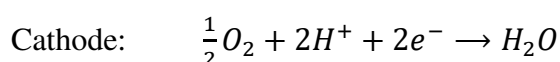
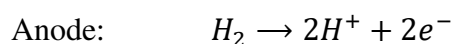
(c) The "natural" variables for the internal energy  $U$  are  $V$  and  $S$ . Show that if  $U(V, S)$  is known, the variables  $T$  and  $P$  may be obtained. Demonstrate that this is not the case starting from  $U(V, T)$ , as follows. Show that

$$\frac{P}{T} = \int \left(\frac{\partial U}{\partial V}\right)_T \frac{dT}{T^2} + f(V)$$

where  $f(V)$  is an unknown function, hence that  $P$  cannot be derived from  $U(V, T)$  and consequently  $U(V, T)$  does not contain complete information about the system.

## 10. Fuel Cell

In a Proton-exchange membrane fuel cell hydrogen gas is supplied to the anode where it forms hydrogen ions (the electrons exit to the electrical circuit) which pass through the membrane to the cathode where they combine with oxygen atoms and electrons that have passed around the external circuit.



The standard enthalpy of formation of water (ie the enthalpy change per mole of water formed for the reaction  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ) is -285.8 kJ/mol at 298K and 1 atm pressure. The standard molar entropies of  $H_2$  (gas),  $O_2$  (gas) and  $H_2O$  (liquid) at 298K and 1atm are 131.0 J/K/mol, 205.0 J/K/mol and 69.9 J/K/mol (liquid).

(a) Why is the standard molar entropy of water much less than that of hydrogen and oxygen.

- (b) Explain why one is interested in the ‘maximum non- $pV$  work’ one can extract from this reaction, and not simply the maximum work. Calculate the maximum non- $pV$  work that can be produced when one mole of liquid water is formed from hydrogen and oxygen gas. Why is this less than the heat produced by burning hydrogen and oxygen to make water??
- (c) Calculate the maximum possible voltage of such a cell.
- (d) What is the maximum possible efficiency (defined as the non  $pV$  work divided by the enthalpy of formation of water) of the cell.
- (d) What limits the efficiency of a practical fuel cell.
- (e) Comment on possible problem issues if such a cell were used to power a car.

## 11. Rubber elasticity

The differential of the internal energy of a thin wire under tension  $f$  and extension  $x$  may be written as

$$dU = TdS + fdx$$

Write down the corresponding differentials for the Helmholtz and Gibbs free energies, and show how the following Maxwell relations may be derived:

$$\left(\frac{\partial S}{\partial x}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_x; \quad \left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial x}{\partial T}\right)_f$$

A rubber band stretched to constant length is found to have a tension proportional to temperature, *i.e.*  $f = g(x)T$ .

- (a) By considering the internal energy  $U$  as a function of  $x$  and  $T$  show that  $\left(\frac{\partial U}{\partial x}\right)_T = 0$  and hence that  $U$  is a function of  $T$  alone.
- (b) By considering  $\left(\frac{\partial S}{\partial x}\right)_T$  show that the entropy decreases when the band is stretched isothermally.
- (c) Show that the temperature of the band increases when it is suddenly (*i.e.* adiabatically) stretched. (Try doing it!).
- (d) What happens if the band is subjected to constant tension, *e.g.* by hanging a weight on it, and heated?

## 12 Surface Tension (1B Physics, Paper 2, 2018)

The differential of the internal energy of a thin film of liquid with surface tension (force per unit length)  $\gamma$  and area  $A$  is  $dU = TdS + \gamma dA$ , where  $T$  is temperature and  $S$  is entropy. Given the corresponding relation for the Helmholtz free energy,  $F = U - TS$ , derive the corresponding Maxwell relation

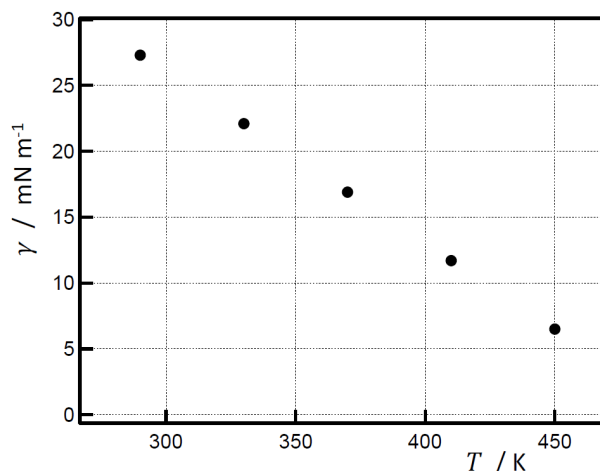
$$\left(\frac{\partial \gamma}{\partial T}\right)_A = -\left(\frac{\partial S}{\partial A}\right)_T.$$

The surface tension of such a liquid is observed to fall with temperature and to be independent of area. Hence show that:

- (a) the entropy rises when the area is increased isothermally;
- (b) the temperature falls when the area is increased adiabatically;
- (c)  $dU = C_A dT + \left(\gamma - T \frac{d\gamma}{dT}\right) dA$ , where  $C_A$  is the heat capacity of the film at constant area.

The surface tension of the film is given by the graph and  $C_A$  is almost constant with a value of  $70 \text{ mJ K}^{-1}$  over the temperature range of interest. Calculate the work done on the film, and the heat supplied to it, when the area is increased  $1 \text{ cm}^2$  reversibly and isothermally at temperature  $330 \text{ K}$ .

Show that in reversible adiabatic changes, the relationship between temperature and area takes the form  $C_A \ln T + \beta A = \text{constant}$ , and determine the quantity  $\beta$ .



Calculate the temperature change if the area of the film is increased by  $1 \text{ cm}^2$  reversibly and adiabatically starting at  $330 \text{ K}$  and comment on the change of internal energy in this process.

### 13. van der Waals' equation

What is the physical basis for the van der Waals' equation of state

$$\left(P + \frac{n^2 a}{V^2}\right) \left(\frac{V}{n} - b\right) = RT$$

Explain the significance of the constants  $a$  and  $b$ . What macroscopic properties of real substances does it account for?

For Argon, the critical point occurs at a pressure and temperature of

$$P_c = 4.83 \text{ MPa} \quad T_c = 151 \text{ K}.$$

Determine values for the van der Waals' constants  $a$  and  $b$  for Argon and estimate the diameter of an Argon atom.

### 14. Phase transitions

(a) Derive the Clausius-Clapeyron equation for the slope of a phase boundary in the  $P$ - $T$  plane of a simple substance in the form  $dP/dT = \Delta S/\Delta V$ . Use it to show that, at low pressures, the vapour pressure of a material has the approximate functional form

$$P = P_0 \exp(-L/RT)$$

where  $L$  is the molar latent heat. Make your approximations clear.

(b) Measurements of the temperature dependence of the vapour pressure,  $P_v$  of carbon tetrachloride give the following data:

$T/^\circ\text{C}$	0	20	40	60	80	100
$P_v/\text{kPa}$	4.3	12.0	28.4	59.3	110.9	192.5

Find the boiling point and latent heat, noting your assumptions.

(c) For hydrogen near its triple point ( $T_T = 14 \text{ K}$ ), the vapour above the liquid phase has a value of  $P_0 = 90 \text{ MPa}$  and a latent heat of evaporation  $L = 1.01 \text{ kJ mol}^{-1}$ . The liquid density is  $71 \text{ kg m}^{-3}$ , the solid density is  $81 \text{ kg m}^{-3}$  and the melting temperature is given by

$$T_m = 13.99 + P/3.3$$

with  $T_m$  and  $P$  measured in K and MPa respectively. Compute the latent heat of sublimation and the slope of the vapour pressure curve for the solid near the triple point.

## Numerical Answers

1 (a) 6/7 atm ; (b) 3350 K, 9.6 atm; (c) 2700 K.

2 (a) 527.5 K; (b) 233 kJ.

3 (a)  $2^{-2/3}T_0 = 0.63T_0$ ; (b)  $\frac{7}{5}T_0$ ; (c)  $T_A = T_0$ ,  $T_B = \frac{5}{3}T_0$  ; (d)  $T_0$  ; (e)  $T_A = 0.76T_0$

6 (a) yes; (b) roughly quadruples.

7 (a) 6.28 J K<sup>-1</sup>; (b) 1.39 J K<sup>-1</sup>; (c) 3.64 J K<sup>-1</sup>; (d) 1.83×10<sup>-5</sup> J K<sup>-1</sup>; (e) 1.83×10<sup>-5</sup> J K<sup>-1</sup>; (f) 0; (g) 0; (h) 5.76 J K<sup>-1</sup>.

8. 400 K

10 (b) -237kJ/mol; (c) 1.228V; (d) 82.9%.

12. Work done =2.2×10<sup>-6</sup>J, Heat transferred = 4.2×10<sup>-6</sup>J, Temperature drop=6.0×10<sup>-5</sup>K

13. a = 0.138 Pa m<sup>6</sup> mol<sup>-2</sup>; b = 3.25 × 10<sup>-5</sup> m<sup>3</sup> mol<sup>-1</sup>; 2.95 × 10<sup>-10</sup> m.

14. (b) 76°C; 29.8 kJ mol<sup>-1</sup>; (c) 1170 J mol<sup>-1</sup>; 11.1 kPa K<sup>-1</sup>.