Department of Chemical and Process Engineering
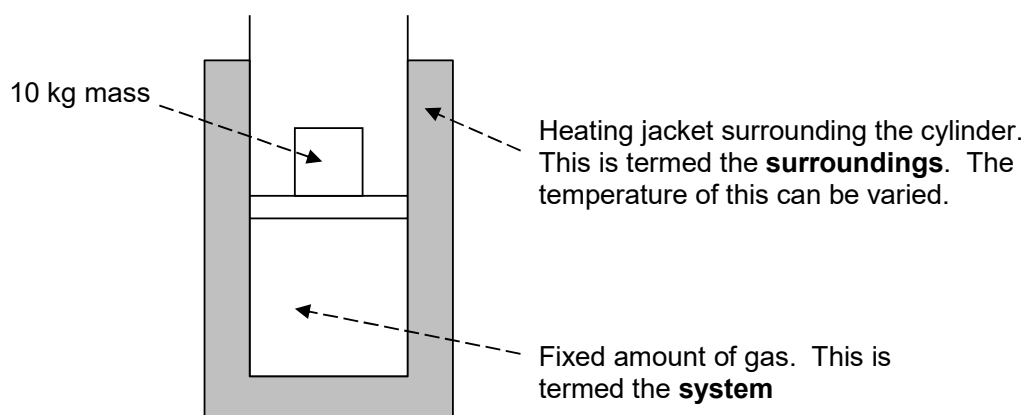**Thermodynamics**

Tutorial Sheet: Heat and Work

1. Calculate the work term when 1 mole of a perfect gas is compressed slowly in a perfectly sealed frictionless piston/cylinder arrangement to half the original volume. The compression can be considered to take place *isothermally* at 25°C.

2. A vertical piston/cylinder arrangement is shown in the picture below. Initially, the cylinder contains 0.2 m³ of air at a pressure of 2 bar (absolute) and a temperature of 300 K. Under these conditions, you can consider that the gas behaves ideally. The piston is held in position by a 10 kg mass. The cylinder is then heated **slowly** and the gas expands until the volume increases to 0.3 m³. This is then the final state of the system.

(a) What is the final temperature (T) and pressure (P) of the system?

(b) Calculate the work (W) done in this process.

(c) What conditions are required to make this a reversible process?

(d) Sketch the process path on a *PV* diagram.

10 kg mass

Heating jacket surrounding the cylinder. This is termed the **surroundings**. The temperature of this can be varied.

Fixed amount of gas. This is termed the **system**

3. A feasibility study is carried out to assess the possibility of separating carbon dioxide, and compressing it at room temperature (300 K) from 1 bar to 20 bar in a steady-flow process for storage. You may assume that the behaviour of the carbon dioxide can be represented by:

$$P(v - b) = RT$$

where b is a term to account for deviations from the perfect gas equation and is equal to 0.00011 m³/mol. You may also assume that the process can be carried out isothermally and reversibly.

(a) Write down the expression for the molar work term in terms of pressure and volume and calculate the molar work of compression. Note that the system is *steady-flow*.

(b) A colleague suggests that it is possible to ignore the b term and assume perfect gas behaviour. What error would this generate? Would this be sensible advice for a compression to 50 bar instead?

4. In a heating process, the temperature of 1 kg of liquid carbon tetrachloride is increased **slowly** from 0°C to 50°C at a fixed external pressure of 1 bar. The coefficient of thermal expansion (α) is 0.0012 K^{-1} and the density at 0°C is 1590 kg/m^3.

Note that in this case, the system is the fixed mass of carbon tetrachloride.

(a) Calculate the work term (W) for this expansion.

1.

$$P = \frac{nRT}{V}$$

$$W = -\int_1^2 P dV$$

$$W = -\int_1^2 \frac{nRT}{V} dV$$

$$= -nRT \left[\ln V\right]_1^2$$

$$= -nRT \left(\ln \frac{V_2}{V_1}\right)$$

$$= -1 \cdot 8.3145 \cdot (25 + 273.15) \left(\ln \frac{1}{2}\right)$$

$$= 1,718.29 \, J$$

In this question we assume that the gas is ideal, that the process is reversible, that the process is a closed system, and that the process is isothermal. These assumptions allow us to use the equation $W = -\int_1^2 P dV$.

2.
In this question we are told that the pressure is held constant at 2 Bar. We will also assume that n is constant, and that the system is reversible because it is carried out slowly.

a)

$$P_1 = P_2$$

$$P = \frac{nRT}{V}$$

$$\frac{nRT_1}{V_1} = \frac{nRT_2}{V_2}$$

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

$$T_2 = \frac{T_1 V_2}{V_1}$$

$$= \frac{300 \cdot 0.3}{0.2}$$

$$= 450 \, K$$

So $P_2 = 2$ Bar, $T_2 = 450$ K.

b)

$$W = -\int_1^2 P dV$$

$$= \left[2 \times 10^5\right]_{0.2}^{0.3}$$

$$= -20,000 \, J$$

c) For this to be a reversible process, it must be carried out slowly so that the pressure of the system can equilibrate with the surroundings for every step of the process. The cylinder must be frictionless to ensure that no energy is lost.

d)
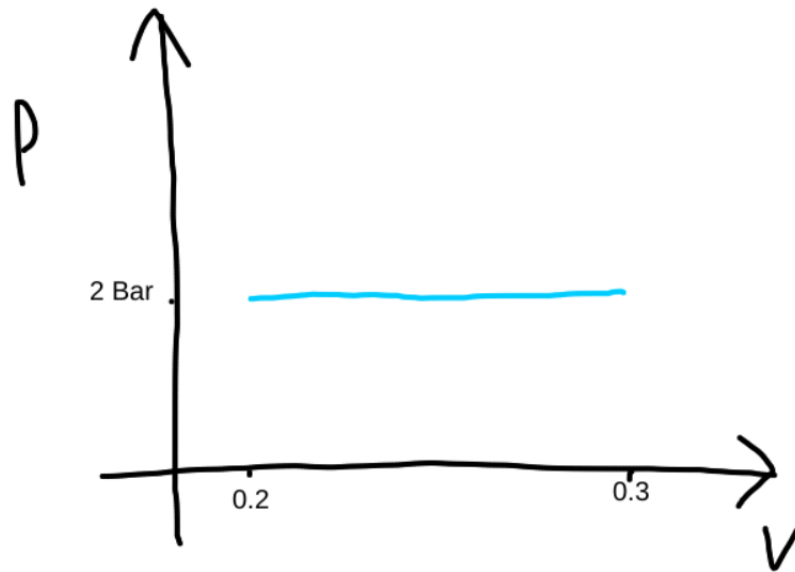
3.
In this question we are told that the process is reversible, steady flow, and isothermal. We are also given the equation $P(v - b) = RT$. We are told that the value of b is $0.00011 \frac{m^3}{mol}$. Note that v is the molar volume.

a)

$$v = \frac{V}{n}$$

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

$$\frac{V}{n} - b = \frac{RT}{P}$$

$$V = \frac{nRT}{P} + bn$$

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

$$\frac{W}{\cancel{n}} = -\cancel{n}\int_1^2 \frac{RT}{P} + b \, dP$$

$$W = [RT \ln P + Pb]_{1\times10^5}^{20\times10^5}$$

$$W = 7,681.37 \, J$$

b)
The ideal gas law is best suited for processes with high temperature and low pressure. Removing the b term will lead to an underestimation in the work. When doing the process at 50 Bar, this pressure would lead to an even greater variation from ideallity making the b term even more important. Neglecting this would be ill-advised.

4.

We assume that this is a reversible process as it is carried out slowly and that the pressure is constant at 1 Bar. We also assume that the density and mass remain constant.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$$

$$V = \frac{m}{\rho}$$

$$\alpha = \frac{\rho}{m}\left(\frac{\partial V}{\partial T}\right)$$

$$\left(\frac{\partial V}{\partial T}\right) = \frac{\alpha m}{\rho}$$

$$\partial V = \frac{(\alpha m) \cdot 50}{\rho}$$

$$= 3.774 \times 10^{-5}$$

$$V_1 = 6.29 \times 10^{-4}$$

$$V_2 = V_1 + \partial V$$

$$V_2 = 6.67 \times 10^{-4}$$

$$W = -\int_1^2 P dV$$

$$W = -\left[1 \times 10^5\right]_{6.29 \times 10^{-4}}^{6.67 \times 10^{-4}}$$

$$= -3.8 \ J$$