Solutions Problem set 1, Thermodynamics 1

Maths warm-up

a) $\int_{x_1}^{x_2} abx^2 \, \mathrm{d}x = \frac{ab}{3}(x_2^3 - x_1^3)$,

b) $\int_{x_1}^{x_2} a \, \mathrm{d}x = a(x_2 - x_1)$,

c) $\int_{x_1}^{x_2} \frac{1}{x} \, \mathrm{d}x = \ln \frac{x_2}{x_1}$,

d) $\int_{x_1}^{x_2} \frac{nRT}{x} \, \mathrm{d}x = nRT \ln \frac{x_2}{x_1}$,

e) $\int_{x_1}^{x_2} \frac{a}{x^2} \, \mathrm{d}x = a\left(-\frac{1}{x_2} + \frac{1}{x_1}\right) = a\left(\frac{1}{x_1} - \frac{1}{x_2}\right)$.

Exercise 1

Isothermal process: T is constant and $\mathrm{d}T = 0$. Perfect gas, hence, the equation of state: $pV = nRT$.

a)

$$dw = -p_{ext}dV \qquad \text{reversible, so} \qquad p_{ext} = p \qquad \text{thus} \qquad dw = -pdV$$

perfect gas such that

$$dw = -\frac{nRT}{V}dV \qquad \text{with} \qquad w = \int \mathrm{d}w = -\int_{V_1}^{V_2} \frac{nRT}{V}dV$$

isothermal, so

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V}dV \qquad \rightarrow \qquad w = -nRT\left(\ln V_2 - \ln V_1\right)$$

$$w = -nRT \ln \frac{V_2}{V_1} \qquad = -2.0 \cdot 8.31 \cdot 323 \ln \frac{25.0}{100} \qquad = 7.44 \text{ kJ}.$$

w is positive, which is in accordance with the fact that the gas is compressed for which work must be done on the system (the gas).

b) We cannot calculate the heat q directly, but it follows from the First Law of thermodynamics:

$$\Delta U = q + w$$

For a perfect *atomic* gas it holds that

$$U = \frac{3}{2}nRT$$

So for an isothermal process in such a gas it applies that

$$\Delta U = 0$$

Therefore,

$$q = -w = -7.44 \text{ kJ}$$

q is negative such that the heat is transferred from the system to the surroundings, which is correct since the increase in temperature as a consequence of compression needs to be compensated in an isothermal process by delivering heat.

Exercise 2

a) Isochoric process so V is constant or $\mathrm{d}V = 0$.

$$\mathrm{d}w = -p_{ext}dV = 0$$

b) Perfect *atomic* gas so

$$\Delta U = \int dU = \frac{3}{2}nR\int dT$$

$$= \frac{3}{2}nR\,(T_2 - T_1) = \frac{3}{2}\cdot 2.0\cdot 8.31\,(350.2 - 300.2) = 1.25\ \mathrm{kJ}$$

Exercise 3

Adiabatic process, so $\mathrm{d}q = 0$ and therefore, $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}w$.

a) For a perfect *atomic* gas it holds that

$$U = \frac{3}{2}nRT,$$

such that for a closed system ($\mathrm{d}n = 0$) U only depends on T, or

$$dU = \frac{3}{2}nRdT.$$

$\mathrm{d}q = 0$ so $\mathrm{d}w = \mathrm{d}U$ and the process is reversible ($p_{ext} = p$) so

$$dw = -pdV = \frac{3}{2}nRdT.$$

b) For p fill in the perfect gas law (equation of state)

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

and we find

$$-\frac{nRT}{V}dV = \frac{3}{2}nRdT$$

or

$$-\frac{dV}{V} = \frac{3}{2}\frac{dT}{T}$$

c) Integration on both sids of this equation results in

$$-\int_{V_1}^{V_2}\frac{dV}{V} = \int_{T_1}^{T_2}\frac{3}{2}\frac{dT}{T}$$

or

$$-\ln\frac{V_2}{V_1} = \frac{3}{2}\ln\frac{T_2}{T_1}$$

From this follows that

$$T_2 = T_1\exp(-\frac{2}{3}ln\frac{V_2}{V_1}) = 323\exp(-\frac{3}{2}\ln\frac{25.0}{100}) = 814\ \mathrm{K}$$

d) From the first law of thermodynamics

$$w = \Delta U = \int dU$$

$$= \frac{3}{2} nR \int dT = \frac{3}{2} nR\Delta T$$

$$= \frac{3}{2} \cdot 2.0 \cdot 8.31 \cdot (814 - 323) = 12.2 \text{ kJ}$$

The work is positive again (compression) but larger than in exercise 1. This is because besides the energy for the compression we now also have to supply the energy for the increase in temperature of the gas; even though in exercise 1 the temperature of the surroundings (the bath) does not change, the bath does take up heat $-q$ to keep the temperature of the system constant; this last point is only possible for an ideal (infinitely large) bath, but this is how we have defined a bath.

Exercise 4

Isobaric process so p is constant or $\mathrm{d}p = 0$.

a)

$$dw = -p_{ext} dV \qquad \text{reversible so} \qquad p = p_{ext}$$

such that

$$dw = -pdV \qquad \text{and thus} \qquad w = -\int_{V_1}^{V_2} pdV = -p(V_2 - V_1)$$

perfect gas so

$$pV = nRT \qquad \text{or} \qquad V = \frac{nRT}{p}$$

With this we find

$$w = -p(\frac{nRT_2}{p} - \frac{nRT_1}{p}) = -nR(T_2 - T_1)$$

$$= -2.0 \cdot 8.31(350 - 300) = -831 \text{ J}.$$

This work is negative so work is done by the system on the surroundings; this is consistent with the fact that we heat the gas at constant pressure so that the volume increases.

b) Perfect *atomic* gas so

$$U = \frac{3}{2} nRT \qquad \text{or} \qquad \Delta U = \frac{3}{2} nR\Delta T$$

$$= \frac{3}{2} nR(T_2 - T_1) = \frac{3}{2} \cdot 2.0 \cdot 8.31(350 - 300) = 1.25 \text{ kJ}.$$

The result for a perfect gas is the same as in exercise 2b since the internal energy of a perfect gas only depends on the temperature (or on the product pV).

Exercise 5

a) The $(p - V)$-diagram is drawn in Figure 1.

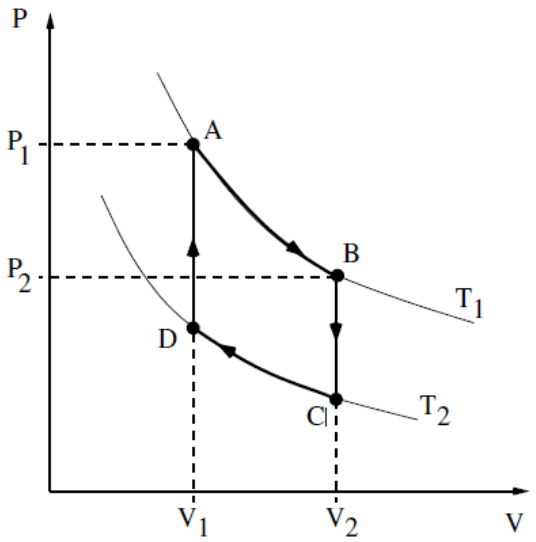


Figure 1: The $(p - V)$-diagram.

b) All four partial processes are reversible, so

$$w = -p_{ext} dV = -p dV$$

We note that $n = 1$, so $V_m = V$, hence, for the real gas we rewrite the equation of state to

$p = RT\left(\frac{1}{V} + \frac{B}{V^2}\right)$, so

$$w_{AB} = -\int_{V_1}^{V_2} p dV = -RT_1 \int_{V_1}^{V_2} \left(\frac{1}{V} + \frac{B}{V^2}\right) dV$$

$$= -RT_1 \left(\ln \frac{V_2}{V_1} - B\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right)$$

$$w_{CD} = -\int_{V_2}^{V_1} p dV = -RT_2 \left(\ln \frac{V_1}{V_2} - B\left(\frac{1}{V_1} - \frac{1}{V_2}\right)\right)$$

$w_{BC} = w_{DA} = 0$ because $dV = 0$ for an isochoric process.

c) $ABCDA$ represents a cyclic process and because U is a state function, the overall change in internal energy must be zero, so $\Delta U = \oint \mathrm{d}U = 0$. The first law then implies $\Delta U = w + q = 0$, such that

$$q = -w = nRT_1 \left(\ln \frac{V_2}{V_1} - B\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right) + nRT_2 \left(\ln \frac{V_1}{V_2} - B\left(\frac{1}{V_1} - \frac{1}{V_2}\right)\right)$$

d) For a perfect gas we would have $B = 0$, implying

$$q = nRT_1 \ln \frac{V_2}{V_1} + nRT_2 \ln \frac{V_1}{V_2}$$

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

$$= nR(T_1 - T_2) \ln \frac{V_2}{V_1}$$

As

$$w = -q$$

$$w = -nR(T_1 - T_2) \ln \frac{V_2}{V_1} = nR(T_2 - T_1) \ln \frac{V_2}{V_1}$$

For the perfect gas the work w is negative as $T_2 < T_1$ and $V_2 > V_1$, so the system (the perfect gas) does work on the surroundings. The magnitude of the work is equal to the surface area in the $(p-V)$-diagram enclosed by $ABCD$, which can be determined by $(\text{area}(ABV_2V_1) - \text{area}(DCV_2V_1))$. Note that the work is $w = -\oint p\mathrm{d}V$ and that the sign of the work depends on the direction of the process ($ABCD$ or $ADCB$).