

## Solutions to home work week 2

1. For ideal gas  $c_V = \frac{dU}{dT}$  and  $c_p = \frac{dU}{dT} + R$ . From the equation of state for one mole of ideal gas  $pV = RT$ , we have for a infinitesimally small change in temperature:

$$dT = \frac{1}{R} [pdV + Vdp] \quad (1)$$

Because of adiabaticity ( $dQ = 0$ ), we have for the change in internal energy

$$dU = -pdV = c_V dT \quad (2)$$

isolating and equating the  $dT$  terms in both expressions gives

$$-\frac{pdV}{c_V} = \frac{1}{R}pdV + \frac{1}{R}Vdp \quad (3)$$

Multiplying by  $c_V$  and using that  $c_p = \frac{dU}{dT} + R$ :

$$-pdV = \frac{c_V}{R}pdV + \frac{c_V}{R}Vdp$$

$$0 = \frac{c_V + R}{R}pdV + \frac{c_V}{R}Vdp$$

$$-\frac{c_V}{R}Vdp = \frac{c_p}{R}pdV \quad (4)$$

$$Vdp = \frac{c_p}{c_V}pdV$$

$$\frac{dp}{p} = -\frac{c_p}{c_V} \frac{dV}{V}$$

to get the changes in  $V$  and  $p$  in going from  $(p_1, V_1, T_1)$  to  $(p_2, V_2, T_2)$  we integrate both sides:

$$\ln \frac{p_2}{p_1} = -\frac{c_p}{c_v} \ln \frac{V_2}{V_1} = \ln \left( \frac{V_1}{V_2} \right)^{\frac{c_p}{c_v}} \quad (5)$$

so that

$$p_2 V_2^{\frac{c_p}{c_v}} = p_1 V_1^{\frac{c_p}{c_v}} \quad (6)$$

2. Because  $S$  is a state function, we can choose always the reversible path for computing the entropy difference. Note that because I forgot to include the temperature the water was at initially, we can't get to a number... For a reversible heating at constant pressure we have that

$$dS = \frac{dQ}{T} = \frac{mc_p dT}{T} \quad (7)$$

with  $m$  the mass of water (1 kg in our example). Integrating both sides

$$\Delta S = mc_p \int_{T_1}^{T_2} \frac{1}{T} dT = mc_p \ln \frac{T_2}{T_1} \quad (8)$$

The heat capacity is so large because of the hydrogen bonding in water.

3. Use that for an ideal gas at constant temperature  $dU = 0$ . Thus, upon reversible expansion

$$dQ = dU - dW = pdV \quad (9)$$

For the entropy change we have

$$dS = dQ/T = \frac{p}{T} dV = R \frac{1}{V} dV \quad (10)$$

Integrating both sides gives the entropy difference in going from  $V_1$  to  $V_2$ :

$$\Delta S = R \ln \frac{V_2}{V_1} \quad (11)$$

- no, because entropy is state function
- For reversible expansion, the entropy of the environment changes by the opposite amount

$$\Delta S_0 = -\Delta S = -R \ln \frac{V_2}{V_1} \quad (12)$$

In this case the entropy change of the total system is zero:

$$\Delta S^{\text{tot}} = \Delta S + \Delta S_0 = 0 \quad (13)$$

- For irreversible work against the constant external pressure at constant temperature we have  $dW = -p_0 dV$ , while  $dU = 0$ . Thus,

$$\Delta Q = p_0 \Delta V \quad (14)$$

so that for the entropy change of the environment

$$\Delta S_0 = -\frac{Q}{T} = -\frac{p_0 \Delta V}{T_0} \quad (15)$$

because  $S$  is a state function,  $\Delta S$  is the same as for the reversible process. Thus for the entropy change in the total system we have that

$$\Delta S^{\text{tot}} = R \ln \frac{V_2}{V_1} - \frac{p_0 \Delta V}{T_0} > 0 \quad (16)$$

The inequality follows from fact that the expansion work is maximal

when done reversibly.

4. During the adiabatic expansion, not only work is done, but also the temperature changes. Thus, we go from  $(p_1, V_1, T_1)$  to  $(p_2, V_2, T_2)$ . We choose again the reversible path. For a reversible process we have that

$$dU = TdS - pdV \quad (17)$$

and for the ideal gas we have that (see 1).

$$dU = c_V dT \quad (18)$$

Isolating  $dS$  in equation 17 and using the expression for  $dU$  from equation 18 we get:

$$dS = \frac{c_V}{T} dT + \frac{p}{T} dV \quad (19)$$

From the equation of state we have that  $\frac{p}{T} = \frac{R}{V}$ . Inserting and integrating on both sides

$$\Delta S = c_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (20)$$

Thus, to get the entropy change, we need to know both the volume and the temperature at the end states. We only know the volumes:  $V_1$  and  $V_2$ . However, in exercise 1 we derived that for *reversible* adiabatic expansion  $pV^\gamma$  is a constant. Because we choose the reversible pathway to do the expansion, we may use that results here (note that this is not true for irreversible adiabatic expansion!):

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad (21)$$

which we can re-write to

$$p_1 V_1 V_1^{(\gamma-1)} = p_2 V_2 V_2^{(\gamma-1)} \quad (22)$$

Using the equation of state for the ideal gas ( $pV = RT$ , assuming one mole throughout):

$$RT_1 V_1^{(\gamma-1)} = RT_2 V_2^{(\gamma-1)} \quad (23)$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{(\gamma-1)}$$

For the ideal gas we also have that

$$\gamma - 1 = \frac{c_p}{c_v} - 1 = \frac{R}{c_v} \quad (24)$$

Therefore,

$$\begin{aligned} \Delta S &= c_v \ln \left(\frac{V_1}{V_2}\right)^{\frac{R}{c_v}} + R \ln \frac{V_2}{V_1} \\ &= -R \ln \frac{V_2}{V_1} + R \ln \frac{V_2}{V_1} \\ &= 0 \end{aligned} \quad (25)$$

Thus, the *reversible* adiabatic expansion is *isentropic*,  $\Delta S = 0$ . The reason is that although we increase volume and do work, we also lower the temperature. This is an example of turning all heat into work!

If not reversible, the final temperature will be higher, and hence entropy increased.